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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

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CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Copper containing Phosphorus. By J. Percy, M.D., F.R.S.; *and on the Corrosive Action of Sea-Water on some Varieties of Copper. By* Captain James, R.E., F.R.S.*

When I had the honour last year of addressing the British Association on the subject of copper smelting, and other metallurgical operations carried on at Swansea and its vicinity, I detailed some experiments on the action of certain bodies on copper. Amongst the illustrations which I presented were specimens of copper, to which, in the state of fusion, phosphorus and arsenic had been added respectively. I showed that, contrary to anticipation, the metal thus treated could be rolled without cracking and drawn out into fine wire, but that by being re-melted *per se* it cracked in innumerable places on being once only passed through the rollers†.

I wish now to direct special attention to the action of phosphorus on copper. On my return from Swansea, I analysed the specimen of copper which I had treated with phosphorus, and found to my surprise that it contained not only a considerable quantity of phosphorus, but also a large proportion of iron, which was doubtless introduced by stirring the copper with an iron rod at the time of adding the phosphorus, which was done several times in succession. The copper employed was the "best selected" of Messrs. Newton, Keates and Co., Liverpool. It was re-cast in a closed flat iron ingot-mould. The ingot was $\frac{1}{4}$ of an inch thick, 5 inches long by 2 broad. It was quite sound, and of a paler colour than ordinary copper. It appeared to be somewhat harder than copper similarly treated with arsenic. As I have already remarked, it rolled well, and might be drawn out into fine wire.

Analysis.—116·76 grs. were digested during many hours in a

* Communicated by Dr. Percy, having been read before the Chemical Section of the British Association, Birmingham, 1849.

† There are many curious practical points in the rolling of metals which are not generally known to chemists.

considerable excess of dilute nitric acid. A comparatively large quantity of black powder remained undissolved. This residuum was washed, dried and ignited. During ignition, it swelled much, and became brown. It was triturated with chlorate of potash and a mixture of carbonate of potash and soda, and heated in a platinum crucible. Some time after effervescence had ceased, the product was treated with hot water, and washed, when a reddish-brown powder remained on the filter. To the solution excess of hydrochloric acid was added, then chloride of magnesium and excess of ammonia. An abundant characteristic precipitate of phosphate of ammonia and magnesia immediately appeared.

The brown powder was dissolved by digestion in nitric acid. The solution, after the addition of an excess of NH^3, was digested with $NH^3, 2HS$. The sulphuret was washed on a filter with water containing $NH^3, 2HS$; the filtrate was digested with excess of HCl until the sulphur had perfectly separated. To the solution, reduced by evaporation, MgCl and NH^3 were added in excess: after thirty-six hours no trace of crystalline precipitate was produced. The black sulphuret was digested in nitrohydrochloric acid, filtered, and precipitated by excess of NH^3; a copious red-brown precipitate of $Fe^2 O^3$ was produced. After ignition, it weighed 2·88 grs, which are equivalent to 1·99 of metallic iron.

There was no appreciable indication of the presence of copper. The supernatant liquor, after precipitation by NH^3, had not a perceptible bluish tint.

The aqueous solution obtained after treatment of the black powder with chlorate of potash and a mixture of carbonate of potash and soda was rendered acid by hydrochloric acid; chloride of magnesium and excess of ammonia were then added. The crystalline precipitate of phosphate of ammonia and magnesia was washed with cold water containing ammonia. By ignition, 3·35 grs. of phosphate of magnesia were obtained, which are equivalent to 2·12 of phosphoric acid or 0·93 of phosphorus.

Examination of the Solution from which the Black Powder was separated by Filtration.—It was treated with excess of HS. An accident occurred in the quantitative determination. However, the solution separated from the sulphuret of copper by filtration was found to contain $Fe^2 O^3$ and PO^5.

From the preceding data we are justified in concluding that the black powder left, after digesting the copper in dilute nitric acid, is a combination of phosphorus and iron. The proportions found on analysis were—

		per cent.
Phosphorus	0·93	31·74
Iron	1·99	68·15
		99·89

Dividing by the respective atomic weights, we have—

$$\frac{31{\cdot}74}{31{\cdot}44}=1, \text{ and } \frac{68{\cdot}15}{27{\cdot}18}=2{\cdot}5.$$

This would give the formula $Fe^3 P^2$, which I think has not been previously described*.

Second Analysis.—A piece of the rolled metal, after scouring with emery, was employed.

Weight, 21·24 grs. It was first digested in nitric acid. Effervescence soon ceased, but the solution continued turbid from the presence of black powder. Hydrochloric acid was then added, and the digestion continued. The black powder was soon dissolved, and a bright green solution obtained. To this a slight excess of potash was added, and then sulphuret of potassium prepared extempore by boiling a solution of potash with flowers of sulphur. Digestion was continued during some hours, after which the precipitate was washed on a filter with water containing some sulphuret of potassium. The filtrate was digested with excess of hydrochloric acid until the excess of sulphur had completely subsided, reduced by evaporation and filtered; chloride of magnesium and excess of ammonia were then added. After standing about forty-eight hours, the precipitate was washed with cold water containing ammonia. It was redissolved by hydrochloric acid, and again precipitated as before. After standing more than twenty-four hours, it was filtered and washed with cold water containing ammonia. By ignition, 1·84 gr. of phosphate of magnesia was obtained, which is equivalent to 2·41 per cent. of phosphorus.

The precipitate obtained by sulphuret of potassium was digested with nitric acid; from the solution, diluted and filtered, the copper was precipitated by HS. The sulphuret of copper was digested with nitric acid, and then evaporated to dryness after the addition of an excess of sulphuric acid. The copper was precipitated by potash. By ignition, 25·47 grs. of oxide of copper (CuO) were obtained, which are equivalent to 95·71 per cent. of metallic copper.

The solution, after precipitation of the copper by HS, was reduced, evaporated and boiled with nitric acid. The iron was precipitated by excess of ammonia. By ignition, 3·48 of oxide of iron were obtained, which are equivalent to 2·41 grs. of metallic iron.

Analysis tabulated.

Copper	95·72
Iron	2·41
Phosphorus	2·41
	100·54

I ascertained the presence of a minute quantity of lead, but its weight was not determined.

It has long been stated that a very small quantity of phosphorus renders copper extremely hard, and adapts it for cutting instruments (Berthier, Traité des Essais, vol. ii. p. 410); but I am not aware that an alloy like that which I have described has been previously mentioned. It is certainly a remarkable fact, that the presence of so large a quantity of phosphorus and iron should apparently so

* These results have been confirmed by my friend T. H. Henry, F.R.S.

little affect the tenacity and malleability of the copper. The effect also of phosphorus in causing soundness in the casting of copper is interesting, and it may be of practical importance. A small quantity of arsenic also, I have remarked, produces a similar result; and a manufacturer of this town recently informed me that he had found the addition of arsenic to an alloy of copper to occasion a most decided effect in promoting the soundness of the metal in casting.

But I have now to introduce another experiment concerning the œconomic use of the compound of copper and phosphorus in question, which has been made by my friend Captain James, of the Royal Engineers, at Portsmouth, and which may possibly become important,—I allude to the protective influence which it appears to exert against the corrosive action of sea-water. I give the results of Captain James' experiments upon various other specimens of copper, under precisely similar circumstances of exposure to sea-water. I wish it to be distinctly understood, that I do not for a moment pretend to draw any decided conclusion from this single result, however carefully it may have been obtained. Yet it appears to be of sufficient importance at least to excite attention to the fact, and to elicit further inquiry, especially when it is remembered how important an œconomic desideratum it is to the Admiralty to diminish or prevent the corrosive effect of sea-water upon copper:—

"Portsmouth, 9th Sept. 1849.

"My dear Sir,—I send you the results of our experiments upon the specimens of copper. The best specimen appears to be No. 3, containing phosphorus, a result apparently the reverse of what you anticipated. In this specimen the surface is perfectly smooth, though tarnished with a green tint which would delight an antiquarian.

"You did not say what specimen No. 5 was; I am therefore in the dark about it; but it appears to be the second-best.

"The dock-yard specimens, you see, are the worst of all.

"Muntz's metal shows its structure by the decomposition of the zinc.

"I think the result on No. 3 so valuable, that I hope you will now see if you can produce some quantity of it, that we may try it on a larger scale.

"Yours truly,
"W. James."

"Dr. Percy."

"*Specimens of Sheet Copper kept constantly in Salt Water for nine months.*

	grains.
No. 1. *Electrotype* (prepared by Mr. Henry Elkington).—	
Original weight	348
Weight after nine months	344½
Loss	3½

Area of specimen, 2½ in. Loss per square inch, 1·4 gr.

grains.

No. 2. Cu + As.—Original weight 323
Weight after nine months 320

Loss 3

Area of specimen, $2\frac{1}{2}$ in. Loss per square inch, 1·2 gr.

No. 3. Cu + P.—Original weight 222
Weight after nine months 222

Loss 0

Area of specimen, $2\frac{1}{2}$ in. Loss per square inch, 0 gr.

No. 4. *From "Frolic."*—Original weight 97
Weight after nine months 80

Loss 17

Area of specimen, 15 in. Loss per square inch, 1·12 gr.

No. 5. *Another variety**.—Original weight ..... $168\frac{1}{2}$
Weight after nine months ..... $164\frac{1}{2}$

Loss 4

Area of specimen, 5 in. Loss per square inch, 0·8 gr.

No. 6. *Dock-yard.*—Original weight 157
Weight after nine months 152

Loss 5

Area of specimen, 3 in. Loss per square inch, 1·66 gr.

No. 7. *Dock-yard.*—Original weight 262
Weight after nine months 253

Loss 9

Area of specimen, 3 in. Loss per square inch, 3 grs.

No. 8. *Dock-yard.*—Original weight ..... $251\frac{1}{2}$
Weight after nine months 245

Loss ..... $6\frac{1}{2}$

Area of specimen, 2·625 in. Loss per sq. in., 2·48 grs.

No. 9. *Dock-yard.*—Original weight 597
Weight after nine months 590

Loss 7

Area of specimen, 3 in. Loss per square inch, 2·33 grs.

No. 10. *Muntz's Metal.*—Original weight 213
Weight after nine months ..... $210\frac{1}{2}$

Loss ..... $2\frac{1}{2}$

Area of specimen, 2·625 in. Loss per sq. in., 0·95 gr."

* I think this was prepared by cementing copper reduced to powder with carbon at or near the melting-point of the metal during many hours, but I am not sure.

I now present two analyses of alloys of copper in reference to the corrosive action of sea-water.

Brass nails used in nailing copper sheathing (alloy of copper and zinc in the proportion usually of 60 to 40) to vessels, and which, although they were cast perfectly sound, became rotten and broke off at the heads after a voyage of a few months to the East Indies.

Method of Analysis.

The alloy was found to consist of copper, zinc and lead. It was dissolved in nitric acid. Sulphuric acid was added in excess, and the whole evaporated to dryness, and heated until the excess of sulphuric acid was completely expelled. The residue was treated with water, which left undissolved sulphate of lead. The copper was precipitated from the solution by sulphuretted hydrogen; the sulphuret of copper was digested with aqua regia, the copper precipitated by potash, and weighed after ignition with the usual precautions. The zinc was precipitated from the boiling solution by carbonate of potash, ignited and weighed:—

	grains.
1. Weight alloy (one nail)	48·64
2. Sulphate of lead	3·37
3. Oxide of zinc	25·01
Repeated. 50·09 grs. of alloy gave of oxide of zinc	25·68
4. Oxide of copper	32·14

Analysis tabulated.

Copper	52·73	
Zinc	41·18	41·06
Lead	4·72	
	98·63	

Nails, which were pronounced to be good, having been removed from a ship's bottom after a voyage to India and back. They were found to contain tin, in addition to copper, zinc and lead. The residue obtained by digestion with nitric acid was estimated, after washing and ignition, as stannic acid. This method is not absolutely exact:—

	grains.
1. Weight of alloy	44·26
2. Stannic acid	1·50
3. Sulphate of lead	5·64
4. Oxide of zinc	13·62
5. Oxide of copper	34·73

Analysis tabulated.

Copper	62·62
Zinc	24·64
Lead	8·69
Tin	2·64
	98·59

Examination of the Crystals of Sugar which occur in the Flowers of Rhododendron ponticum. *By* Dr. B. Stamer.

Fourcroy and Vauquelin were the first who observed that the flowers of *Rhododendron ponticum* secrete a solid honey, which resembles candied sugar and melts during the night; the same observation was made subsequently by Henslow. The sugar has been more minutely described by Jäger. It was perfectly white, granular, gritty between the teeth, with a taste of common sugar; specific gravity $=1{\cdot}56$; readily soluble in water, but sparingly soluble in alcohol of 0·808 spec. grav. even when heated.

The author has submitted this sugar to a more accurate examination. The specimen consisted of small roundish granules about the size of hemp-seed; it was hard, perfectly white, of a pure sweet taste; furnished a perfectly white and dry powder, and dissolved readily in water and in dilute alcohol; the solutions were neutral and clear. When heated upon platinum, it carbonized, giving off the characteristic odour of caramel; and left a shining black coke, which on continued ignition burnt, leaving scarcely any residue.

Towards reagents it behaved as follows:—A sample, dried at 212° and then mixed with sulphuric acid, turned first yellow, then brown, and at last black. On boiling a solution of this sugar in water with potash, it remained almost colourless, exhibiting merely a faint reddish tint. Sulphate of copper was added to the solution, and then caustic potash, until the precipitate redissolved with an azure-blue colour. It was then heated nearly to boiling, but no change resulted, and after long-continued ebullition no red protoxide of copper separated. Dissolved in a little water mixed with caustic potash and heated to boiling, an addition made of nitrate of cobalt produced immediately a bluish-violet precipitate. On adding a little yeast to a solution of this sugar in a small flask, and passing the tube for conveying the gas into lime-water, a disengagement of gas set in in the course of a few hours, and the gas precipitated the lime as carbonate. By drying in the water-bath, this sugar lost only 0·055 per cent. of water. On combustion, it left 0·026 per cent. of ash. The sugar, dried at 212°, gave on analysis—

Carbon	41·93	12	42·10
Hydrogen	6·39	11	6·44
Oxygen	51·68	11	51·46

It is evident therefore that the sugar of the flowers of *Rhododendron ponticum* is pure cane-sugar. The amount of inorganic substances mixed with it was so small, that it was found impossible to ascertain their nature; no precipitate was produced in the solution of the sugar by nitrate of silver, chloride of barium, nor by oxalate of ammonia.

In Tournefort's "Journey to the Levant," it is stated that the honey collected by bees from *Rhododendron ponticum* possesses narcotic properties. The author has not been able to detect any such substance; the distillate from the sugar with water was perfectly

neutral, void of colour and taste; nor could a trace of nitrogen be discovered on burning the substance with soda-lime, and collecting the gases in muriatic acid.—*Archiv de Pharm.*, lix. p. 151.

On the Occurrence of Formic Acid in Stinging Nettles. *By* Dr. Gorup-Besanez.

Some time ago, F. Will showed, by microchemical and microscopical experiments, that the fluid in the hairs of the so-called procession-caterpillar (*Bombyx processionaria*), which causes an inflammation of the skin, as well as the liquid in the poisonous organs of some insects, is nothing else than formic acid. It became highly probable therefore that formic acid would also occur in the vegetable kingdom already formed; and the first class of plants which was thought of was that which, by means of stinging hairs or similar organs, produces an analogous effect to the sting of certain insects.

About a pound of the collected plants, *Urtica urens* and *dioica*, was cut small and pressed, and submitted to distillation with about four times the quantity of water and a few drops of concentrated sulphuric acid. The distillate was opalescent; a few oil-drops floated on its surface; it had a very offensive odour and a scarcely perceptible acid reaction. Mixed with carbonate of soda and evaporated to dryness in the water-bath, it furnished a brownish mass, a very small portion of which was deliquescent, the greater part consisting of the excess of carbonate of soda.

This mass was now very cautiously decomposed in a glass retort by the gradual addition of dilute sulphuric acid, when a distinctly acid distillate was obtained in the well-cooled receiver, which, neutralized with ammonia, gave all the reactions characteristic of formic acid. This experiment however did not appear to me to furnish a satisfactory proof of the presence of ready-formed formic acid in the plant, as formic acid can be *produced* from the most different organic substances by concentrated sulphuric acid; and it was possible that in the present case the formic acid might have been produced by decomposition towards the end of the operation.

5 lbs. of stinging nettles were therefore distilled with a corresponding quantity of water without any addition of sulphuric acid, and a product obtained perfectly similar to the one above mentioned. It was neutralized with carbonate of soda, evaporated to dryness, the residue decomposed with dilute sulphuric acid, and the acid distillate digested with carbonate of lime, in order to avoid the excess of carbonic acid and excess of alkali, which rendered the reactions very indistinct, and filtered. The yellowish solution, concentrated in the water-bath, proved to be formiate of lime. It reduced salts of silver and mercury, gave with sulphuric acid the characteristic odour of formic acid, and with sulphuric acid and alcohol the still more characteristic smell of formic æther; oxalate of ammonia showed the presence of lime.

The amount of formic acid present in stinging nettles is certainly small; but this will not appear surprising, if we suppose that

this acid is contained only in the stinging hairs, an assumption which is confirmed by the microscopic observations of Will and Lucas. When, for instance, solution of silver is added to the plant under the microscope, and a gentle heat applied, reduction always first occurs at the extremity of the stinging hair.—*Journ. für. Prakt. Chem.*, xlviii. p. 191.

On the Action of some Acids and some Acid Salts on White Precipitate (Chloro-amidide of Mercury). *By* C. Kosmann.

Although the white precipitate has been the object of a great number of investigations made by the most distinguished chemists, as Soubeiran, Mitscherlich and Kane, and its amidic nature, established first by the latter chemist, has thrown considerable light on this compound, by placing it in some measure by the side of Gros and Reiset's bases, I have nevertheless thought that the following experiments will merit the attention of chemists.

Action of Sulphuric Acid on White Precipitate.—I boiled some white precipitate (obtained by precipitating, at a temperature of 61° F., chloride of mercury by solution of ammonia, washing and drying the precipitate) in water rendered acid by sulphuric acid in sufficient quantity to dissolve the substance entirely. The filtered liquid was evaporated on the bath until it furnished white laminar crystals, which were separated from the mother-liquor, and pressed about a dozen times between folds of blotting-paper until perfectly dry.

For analysis, 2·533 grms. of the salt were dissolved in distilled water to which a few drops of nitric acid had been added, and then sufficient water to form 99 cub. centim.; 33 cub. centim. of this liquid were employed for the determination of the amount of chlorine by nitrate of silver. A second 33 cub. centim. were mixed with chloride of barium, and the amount of sulphuric acid deduced from the precipitated sulphate of baryta. The other 33 cub. centims. having been lost, I weighed off 0·843 grm. of the salt, and added to it an acidified solution of protochloride of tin. After the addition of a little water, I boiled, and soon obtained globules of mercury, which were dried and weighed. The following were the numbers obtained:—

		Calculated.
Sulphuric acid	18·156	16·41
Mercury	60·915	62·13
Chlorine	13·233	14·48
NH^4	4·072	3·71
Oxygen.....	3·624	3·27

leading to the formula $2(SO^3, HgO)\,Cl, NH^4 + ClHg$. This double salt having been crystallized but once, retained a little sulphuric acid, whence the excess of this acid in the analysis. Its binary elements are not very strongly combined, for æther removes the whole of the ClHg, which is then readily obtained by evaporation. The following equation readily explains the formation of this double salt:—

$$4(SO^3)+2(ClHg+HgNH^2)+4HO=$$
Chloro-amidide of mercury.
$$2(SO^3\,HgO)+(ClNH^4+ClHg)+SO^3\,HgO+SO^3,NH^4\,O.$$

In fact, the mother-liquor contains a salt composed of sulphate of ammonia and sulphate of mercury. The salt, analysed, might therefore be regarded as the sulphate of the chloro-amidide of mercury combined with chloride of mercury; it might also be looked upon as formed of 2 equivs. of sulphate of mercury and 1 equiv. of alembroth salt.

It turns yellow on being treated with water, depositing a basic sulphate. Potash liberates a considerable amount of ammonia.

Nitric Acid and White Precipitate.—When placed in contact with water containing a large amount of nitric acid, the action is very feeble in the cold; but when the mixture is heated, the white precipitate dissolves slowly and entirely. The filtered liquid yields on evaporation an abundant crop of white laminar crystals (A) with a silvery lustre. The mother-liquid, on further evaporation, furnished some small oblique prisms, likewise of a metallic lustre. For examination, the crystals were dried perfectly between folds of blotting-paper, and were then submitted to the following tests:—

The crystals A did not dissolve in water, but rendered it milky; with caustic potash and the assistance of heat, a small quantity of ammonia was disengaged; tincture of indigo and sulphuric acid, or a crystal of the protosulphate of iron and sulphuric acid, proved the presence of nitric acid; the chlorine and the mercury are readily detected; æther deprives it of a large quantity of chloride of mercury, which it deposits in beautiful needles. It furnished—

		Calculated.
Mercury	64·096	64·680
Chlorine	22·333	22·610
Nitric acid	9·153	8·534
Oxide of ammonium	4·419	4·176

leading to the formula $4ClHg+NO^5+NH^4\,O$.

The double salt of the second crystallization, treated with æther, parts with a small quantity of chloride of mercury; the residue, insoluble in æther, is very sparingly soluble in cold water; potash disengages from it a large quantity of ammonia; it also contained mercury and nitric acid in considerable quantity, and is consequently a combination of a little chloride of mercury with a large amount of ammonio-nitrate of mercury. It was not analysed quantitatively. The action of dilute nitric acid upon the chloro-amidide of mercury consists in oxidizing and dissolving the amidide of mercury, forming nitrate of ammonia and nitrate of mercury. 1 equiv. of the former combines with 4 equivs. of the chloride of mercury, separated from the chloro-amidide, and crystallizes first. The salt remaining in the mother-liquor was consequently composed of all the nitrate of mercury, of a great portion of the nitrate of ammonia, and a small portion of chloride of mercury.

Chloro-amidide of Mercury, Hydrochloric Acid and Chloride of Sodium.—I took—

Chloro-amidide of mercury	8·00
Crystallized chloride of sodium	8·00
Hydrochloric acid	6·00
Distilled water.....	120·00

I heated the liquid, when the whole dissolved. It was filtered and slowly evaporated, when it deposited some white cubic crystals, which were redissolved and crystallized a second time. On testing them, they proved to contain only sodium and chlorine, no ammonia and no mercury.

The mother-liquor furnished some yellowish crystals, which on recrystallization were obtained in beautiful white quadrilateral laminæ with two sides broader than the other two, or in flattened parallelopipeds with a metallic lustre. They gave on analysis—

	Found.	Calculated.
Mercury	35·041	36·051
Chlorine.....	43·763	44·141
Sodium	15·0175	16·572
Ammonium	4·4432	3·236
Loss	1·7353	

These numbers lead to the formula $2ClHg + ClNH^4 + 4ClNa$, or a direct combination of hydrochloric acid with the chloro-amidide of mercury +4 equivs. chloride of sodium.

This double salt is soluble in water; ammonia produces no precipitate in it; caustic potash disengages ammonia.

Binoxalate of Potash and White Precipitate.—In order to determine the chemical action of these two substances on each other, I boiled together 2 parts of binoxalate of potash, 1 ammoniacal white precipitate, with a sufficient quantity of distilled water, until no more was dissolved; there remained a perfectly insoluble deposit, A, whilst carbonic acid was disengaged, which was passed into a solution of chloride of barium mixed with pure ammonia, in which it produced a precipitate of carbonate of baryta.

The white deposit, A, insoluble in the boiling liquid, was washed and placed in contact with some liquid ammonia; a black precipitate of suboxide of mercury was immediately formed. The filtered ammoniacal liquid was neutralized with nitric acid, and then treated with nitrate of silver; the precipitate thus formed dissolved in ammonia and in nitric acid; the neutralized ammoniacal liquid furnished a white precipitate with chloride of calcium, insoluble in acetic acid; it is therefore oxalic acid, and the white deposit is the oxalate of the suboxide of mercury.

The liquid separated from the white deposit A was exposed to the rays of the sun, which almost immediately caused a formation of subchloride of mercury.

The first action of the binoxalate of potash on white precipitate consists therefore in 1 equiv. of the chloro-amidide of mercury and 2 equivs. water losing 2 equivs. of oxide of mercury; the

one yields its oxygen to 1 equiv. C^2O^3, to form $2CO^2$; the other combines with the mercury to form Hg^2O, which unites with the $2(C^2O^3)+KO$, producing C^2O^3+KO and $C^2O^3+Hg^2O$; C^2O^3+KO remains in solution; $C^2O^3+Hg^2O$ separates in a pulverulent state; there likewise remains in solution Cl, NH^4.

The second action, which is parallel to the first, consists in 2 equivs. of the binoxalate of potash reacting upon 1 equiv. of white precipitate, forming potassio-oxalate of ammonia and potassio-oxalate of mercury and chloride of mercury; these three substances remain in solution; but then comes the action of light, which decomposes the potassio-oxalate of mercury; the oxygen of 1 equiv. of HgO combines with C^2O^3, forming $2CO^2$, which is liberated; the Hg unites with ClHg, and forms $ClHg^2$, which is deposited in white flakes; $2(C^2O^3)+KO+NH^4O$ and C^2O^3, KO remain in solution. The following equation exhibits this reaction:—

$$4(C^2O^3)+2KO+(ClHg\,HgNH^2)+2HO=2CO^2+ClNH^4 +2(C^2O^3KO)+C^2O^3Hg^2O,$$

and by the action of the light,

$$4(C^2O^3)+2KO+(ClHg\,HgNH^2)+2HO=ClHg^2 +2CO^2+C^2O^3,KO+2(C^2O^3)KO+NH^4O.$$

Bitartrate of Potash and Chloro-amidide of Mercury.—I boiled a mixture of 60 parts bitartrate of potash and 20 parts ammoniacal white precipitate with sufficient distilled water until the whole mass was nearly dissolved; a pretty large quantity of CO^2 was disengaged, and a yellow residue, mixed with undecomposed white precipitate and subchloride of mercury, remained. I filtered the boiling liquid; on cooling, a salt of mercury separated, which was redissolved in the liquid by ebullition; on evaporating again until the appearance of a pellicle, I obtained a new salt of mercury, A, mixed with cream of tartar. The mother-liquor separated from these crystals deposited on evaporation a salt that I shall call B. The mother-liquor, on further evaporation, furnished a salt in yellow acicular crystals, C.

All these salts turn gray when exposed to the light, dissolve with difficulty in water, and give a yellow precipitate with caustic potash. In the boiling a large quantity of carbonic acid was disengaged, arising from the decomposition of the tartaric acid.

The salts A, B and C yielded, on qualitative analysis, tartaric acid, chlorine, mercury and potash, but no ammonia. After the crystallization of the salt C, the residual liquid furnished crystals in thin tablets, soluble in water; they contained tartaric acid, potash, ammonia and chlorine, but not a trace of mercury. I shall designate this salt by D.

The salt C furnished on analysis—

	Found.	Calculated.
Potash	16·840	16·593
Mercury	17·580	17·801
Chlorine	6·059	6·224
Tartaric acid	..	46·728
Water	..	12·654

As this double salt turns quickly black in the light, it has probably the following constitution :—$\overline{T}^2HgO+\overline{T}^2KO+ClK+8HO$.

The salt D was very soluble in water immediately after its preparation, had a saline taste, and disengaged a large quantity of ammonia when treated with caustic potash. Having left it for fifteen days exposed to the air in a capsule covered with paper, I made only a qualitative analysis of it; its taste had become slightly acid; it was no longer entirely soluble in cold water, and disengaged scarcely any ammonia when treated with potash; it had lost its ammonia, just as the tartrate of potash and ammonia does when exposed to the air. From 100 parts I obtained—

Potash	28·710
Chlorine.....	3·247

The remainder was tartaric acid and ammonia. It was therefore a mixture of ammonio-tartrate of potash with chloride of ammonium and neutral tartrate of potash. In this reaction the bitartrate of potash assimilates a portion of chloride of mercury, and forms a sparingly soluble double salt, which is deposited in crystals.

The amide of mercury, $HgNH^2$, is decomposed on combining with the oxygen and hydrogen of the water in order to form oxide of mercury and ammonia; the first is deposited, the second unites with a portion of bitartrate of potash. Another portion of the chloro-amidide of mercury is decomposed in a different manner. The amide of mercury, $HgNH^2$, decomposes water; it combines with the H to form NH^3; the oxygen is used to burn a portion of the tartaric acid, whence the production of CO^2 and the Hg of the amide of mercury combines in the nascent state with ClHg to form $ClHg^2$, which is observed in the deposit mixed with an excess of white precipitate and oxide of mercury.

Acetic Acid and Chloro-amidide of Mercury.—I boiled some white precipitate with an excess of acetic acid. The flask which contained the mixture was provided with a tube bent twice at right angles, the longest arm of which dipped into an ammoniacal solution of chloride of barium. On ebullition, a precipitate of carbonate of baryta was formed in the barytic solution; the liquid had entirely dissolved the white precipitate; but a fresh precipitate had formed in the boiling liquid, which no longer disappeared. After having filtered the liquid and collected this white deposit on a filter, it was washed; heated with ammonia, it became black and deposited suboxide of mercury. The filtered ammoniacal solution contained chloride of ammonium; the deposit therefore was subchloride of mercury.

The filtered liquid separated from the $ClHg^2$ was evaporated in a hot chamber; it deposited yellowish crystalline crusts, which were separated, pressed between bibulous paper until perfectly dry; then left for some time exposed to the air, during which time they diffused a strong odour of acetic acid, and were readily blackened by light. They contained acetic acid, mercury, chlorine and ammonia; they were almost entirely insoluble in water, pretty soluble in hot

acetic acid; soluble, after continued boiling, in dilute nitric acid, and did not part with anything to æther. These yellowish crystals furnished on analysis—

Mercury	72·860
Chlorine	13·046
Oxide of ammonium	6·687
Oxygen	5·753
Acetic acid	3·085

The formula of the hexabasic acetate of the chloro-amidide of mercury + 12 equivs. water, or of the hexabasic acetate of the ammoniacal oxychloride of mercury, requires the following numbers:—

Mercury	72·158
Chlorine	12·616
Oxide of ammonium	6·468
Oxygen	5·703
Acetic acid	3·055

The reaction of these two substances on each other is very simple; the oxygen of 1 equiv. of water goes to a portion of acetic acid and produces carbonic acid, whilst the hydrogen goes to the amide of mercury and forms ammonia, which combines with a portion of acetic acid. The acetate of ammonia formed is volatilized during the evaporation; but the mercury of the amide combines in the nascent state with the subchloride of mercury, and is deposited as chloride.

Another portion of the chloro-amidide of mercury combines directly with water and acetic acid, like a weak base, which parts with the greater portion of the acetic acid during the evaporation, not retaining more than 3 per cent.

Chloro-amidide of Mercury, Sulphate of Quinine and Sulphuric Acid.—Having by mistake mixed some white precipitate with sulphate of quinine, I tried to separate them without the use of alcohol, and triturated the mixture in distilled water; I added a slight excess of weak sulphuric acid, when a great portion dissolved. Supposing I had bisulphate of quinine in solution, I filtered, and tested the liquor for mercury, and was surprised to find it contained a considerable amount of that metal. This led me to suppose that a double salt had been formed, and was the starting-point of this investigation.

I evaporated the solution, and obtained a confusedly crystalline salt, which was frequently treated with alcohol of 85°, which dissolved the greater portion; the alcoholic solution, filtered and evaporated, left a confusedly crystalline salt, which still contained a considerable quantity of mercury. The results of the analysis approach closely to the formula—

$$12SO^3 + 6 \text{ quinine} + SO^3 + ClHg\,HgN^2 + 2HO,$$

or 12 equivs. bisulphate of quinine + 1 equiv. sulphate of the chloro-amidide of mercury + 2 equivs. water.

This double salt has a metallic bitter taste; dissolves with difficulty in water, more readily in alcohol. When the mercury has been separated by sulphuretted hydrogen, it furnishes on evaporation crystals of pure sulphate of quinine.—*Ann. de Chim.*, Nov. 1849.

Observations on Ozone and Black Phosphorus. By G. Osann.

When ozonized air is passed into a solution of oxide of lead in solution of potash, a yellow precipitate is obtained, which acquires a reddish colour on drying, and appeared from analysis to be nothing more than that modification of oxide of lead which Mitscherlich obtained by pouring a concentrated solution of a lead salt into a boiling paste of hydrate of lime and water, and continuing the ebullition until the precipitated oxide of lead had become converted into a heavy red powder.

When ozonized air is passed for a considerable length of time over fragments of phosphorus, they become black. This blackening appears to be owing to the presence of copper in the phosphorus, which Osann detected on this occasion. Black phosphorus is easily obtained according to the following method:—Red oxide of phosphorus is procured by burning phosphorus fused under water with oxygen gas, and treating it with phosphoric acid. The red oxide so obtained is boiled with concentrated phosphoric acid. It thereby soon changes its colour and its bulk, and assumes a blackish-gray appearance. On continued boiling, a black powder separates, whilst the mass becomes grayish-brown; the brown mass is removed and digested in nitric acid, when it dissolves with a blue colour, owing to the presence of copper.

Again, when ozonized air is passed through a solution of nitrate of silver in ammonia, a black precipitate forms. This precipitate yielded on reduction in hydrogen 97·56 per cent. silver to 2·44 oxygen; so that an oxide of silver of the composition Ag^3O appears to exist, which has consequently a different composition from the protoxide of silver discovered by Wöhler (Ag^2O). If the ammoniacal nitrate of silver solution is exposed to the air, there is formed in the course of a few weeks a thin saline crust at the margin of the liquid, which is blackened, and apparently contains the same oxide. This phænomenon exactly corresponds with the behaviour of starch moistened with a solution of iodide of potassium, which likewise turns blue in time by exposure.

Osann has examined more closely ozonized air, and that saturated with white vapours, as obtained by passing air over phosphorus, transmitting it first through a solution of iodide of potassium, and then, when freed in this manner from ozone, collecting it in a glass vessel. As soon as this was filled, the operation was discontinued. After about twenty-four hours the white vapour had disappeared, and the water closing the bell-glass had an acid reaction. Mixed with lime-water no precipitate resulted; but on boiling the liquid a white powder separated, whence it follows that this substance is phospho-

rous acid. It would at the same time follow that there are two modifications of phosphorous acid; one of which resists combination with water, the other not.

Now if ozone is only a modification of oxygen (active oxygen), it must be distinguished from the passive modification in the same manner as is done for these conditions in other bodies. The same would also apply to phosphorous acid; and it would then be worthy of remark, that in the preparation of ozone by means of oxygen, the phosphorous acid is converted into the passive, and the oxygen into the active modification.—Poggendorff's *Annalen*, lxx. p. 592.

New Process for determining the Proportion of Sulphate of Cinchonine which exists in the Sulphate of Quinine of Commerce. By O. Henry.

This process is based on the great difference of solubility in cold water of the acetates of the two alkaloids. I take 10 grms. of the suspected sulphate, add 4 grms. of acetate of baryta, and triturate very carefully in a porcelain mortar with 60 grms. of pure water to which a few drops of acetic acid have been added. The mixture soon forms a thick silky mass, occupying a considerable volume. It is carefully moved with an ivory knife on to a piece of fine linen, quickly expressed, and the turbid liquid resulting from the expression filtered through paper into a flask, diluted with twice its volume of alcohol of 35°, after having previously added a slight excess of sulphuric acid and filtered it again*. A decided excess of caustic ammonia is then added, and the whole boiled for a few minutes. The ebullition soon causes the separation of crystalline flakes, which when plentiful quickly subside, producing a deposit of acicular crystals of pure cinchonine. The liquid is allowed to cool; the crystals or the granular deposit are carefully collected on a weighed filter and after having quickly dried them at a suitable temperature, the quantity of the precipitate is weighed; it represents within one-seventh or one-eighth the amount of sulphate of cinchonine existing in the quinine. The alcoholic liquid, collected separately, furnishes on evaporation acetate of quinine. Thus a complete examination of the suspected sulphate may be made without loss.

With known mixtures of pure sulphate of quinine with one-fifth, one-tenth and one-twentieth of sulphate of cinchonine, I have obtained by this method very approximative results, although always slightly below the quantities added.

In commerce, Liebig's process is usually employed for ascertaining the purity of sulphate of quinine. It consists in triturating 1 grm. of the sulphate, selected from a number of specimens, in a porcelain

* In this manner the whole of the cinchonine is collected as acetate and the greater portion of the quinine removed, which is very important; for on precipitating the cinchonine by ammonia, if it is nearly pure the deposit is crystalline, but if there is much quinine it is viscous and resinous.

mortar, with 60 grms. of pure ammonia; transferring it into a flask, and mixing with the milky liquid 60 grms. of sulphuric æther. The well-stoppered flask is repeatedly shaken, and then set aside. The quinine dissolves in the æther with a perceptible trace of cinchonine; but the greater portion of the latter floats in the form of white crystalline flakes, or as a crystalline powder between the ætherial and ammoniacal liquids. The quantity is estimated approximatively by the eye and by comparison with a normal solution.

This very ingenious process, which is easily executed, has nevertheless one inconvenience; it does not admit of the separated cinchonine being accurately collected and weighed; moreover, the price of æther is another objection. This is avoided by the process I have proposed.—*Journ. de Pharm.*, Nov. 1849.

Impurity in Oxygen from Chlorate of Potash. By Dr. Vogel.

The author has observed that the oxygen disengaged from chlorate of potash contains chlorine. The same observation has been made by Prof. Poggendorff, and more recently by Chevreul. The author found, that the salt, when it has been repeatedly crystallized, furnishes a purer gas, and ascribes the disengagement of chlorine to the presence of some perchlorite in the chlorate.—Buch. *Rep.*, vol. iii. p. 145.

On the Extraction of Gold from the Copper Ores of Chessy and Sain-Bel. By Messrs. Allain *and* Bartenbach.

It results from our experiments, that at least two ten-thousandths of gold may be extracted from the above copper ores, the working of which, as the mines in question are of considerable extent, may become highly important. The density of the ore being 4, 1 cubic metre represents 800 grms. of gold. The operations are easy and rapid, and consist in first roasting the ore, and then dissolving out the gold.

After the mineral has been roasted in small fragments in the air, with a view to render it more friable, it is pulverized, passed through a fine brass sieve, and again roasted as much as possible, that is to say, until the powder has acquired a homogeneous brownish-red colour. It is then formed into a paste with sulphuric acid of 66°, and roasted a last time until there is no further disengagement of sulphurous or sulphuric acid. The employment of sulphuric acid is most efficacious, as on the one hand, the sulphur in the form of sulphuric acid serves to remove sulphur, and on the other, as this metalloid, on becoming oxidized either by the air or at the expense of the oxygen of its compound, furnishes a greater amount of sulphuric acid than is wanted if the sulphurous vapours of the different roastings are passed into leaden chambers. Again, sulphuric acid is preferable for removing the oxides of zinc and copper formed,

as it readily converts the last traces of sulphurets which may have escaped the roasting into sulphates.

The substance is then reduced to as fine a powder as possible, and boiled with weak sulphuric acid. The insoluble portion is washed, and lastly heated with aqua regia diluted with water, but having been previously made in the proportion of 6 parts of hydrochloric acid of 21° and 1 part of nitric acid of 36°. This is an important point. The liquid containing the chlorides of iron, gold (and even of copper, for it is difficult to remove this metal entirely by a single ebullition with sulphuric acid), is placed in contact with iron, which precipitates the gold and copper; the precipitate is collected, washed, dried and calcined, to oxidize the copper. The gold may be separated from the oxide of copper and oxide of iron (for there is always a little of the latter precipitated in the cementation) by sulphuric or hydrochloric acid; but the separation, either by fusion or by chlorine or mercury, is preferable. With the chloride the metal is reduced by heat, with amalgam the mercury is volatilized. The process above described is applicable to all pyrites which contain gold. The expenses attending the extraction of 2 lbs. of gold from the Chessy ores, after deducting the value of the copper obtained, do not exceed four hundred francs.—*Comptes Rendus*, Nov. 19, 1849.

ANALYTICAL CHEMISTRY.

Observations on the Estimation of Lime. By Alvarro Reynoso.

One of the operations which chemists have frequent occasion to perform is the estimation of lime; and as it is always made in the state of oxalate of lime, it is important to know all the properties of that salt, to avoid errors in the analysis. With this object I have undertaken some experiments on the action of soluble salts, capable of forming insoluble oxalates by acting upon the oxalate of lime.

Under the influence of a soluble salt of copper (chloride, sulphate, nitrate), the oxalate of lime is converted into oxalate of copper; the presence of lime was proved in the liquid separated from the oxalate of copper. The precipitate formed by mixing 1 equiv. of chloride of calcium with 1 equiv. oxalate of ammonia, dissolves in chloride of copper when poured into it all at once; but after long standing, agitation or ebullition of the liquid, a precipitate is formed, which furnishes on analysis the composition of the oxalate of copper; when the chloride of copper is added by degrees, the oxalate of lime is converted into oxalate of copper, and there is formed at the same time a soluble salt of lime; the oxalate of copper is precipitated, and no longer redissolves in an excess of chloride of copper. The fact of the solution of the oxalate of lime in chloride of copper, and of the

subsequent precipitation of oxalate of copper, appears to be analogous to what takes place when ammonio-phosphate of magnesia is formed in the presence of a large excess of hydrochlorate of ammonia. This property does not belong exclusively to the chloride of copper, as other salts (chloride of calcium, chloride of ammonium and chloride of sodium) equally retard the precipitation of the oxalate of copper.

The oxalate of lime, in presence of a large excess of some salts (chloride of sodium, chloride of calcium and chloride of ammonium), dissolves in the chloride of copper even when poured into it drop by drop; however, in this case, it is necessary to guard as much as possible against any vibration, which occasions the formation and precipitation of the oxalate of copper, which no longer dissolves in the excess of the copper salt; the precipitate, however, is formed after a certain time.

When an excess of oxalate of ammonia is poured into chloride of calcium, and a salt of copper then added, no solution takes place; a precipitate of oxalate of copper is obtained, and a soluble salt of lime exists in the liquid; but if this experiment is made in the presence of an excess of muriate of ammonia, the oxalate of copper is not precipitated immediately, but the solution remains clear for some time.

Oxalate of lime, boiled with soluble salts of silver, lead, cadmium, zinc, nickel, cobalt, strontia and baryta, undergoes double decomposition, a soluble salt of lime being formed and a precipitate of oxalate of the above metals.

Thus the oxalate of lime is decomposed by all the soluble salts of metals capable of forming insoluble oxalates and soluble salts of lime. The decomposition is effected the more perfectly the higher the equivalent of the metal replacing the lime.—*Comptes Rendus*, Nov. 12, 1849.

On the Separation of Phosphoric Acid from Alumina.
By H. Rose.

The author recently published a method* upon separating phosphoric acid from bases by means of mercury, which admits of the phosphoric acid being separated from most of the bases in such a manner, that not only its quantity can be determined with great accuracy, but that after its separation the bases can be readily examined and accurately estimated, without being contaminated by the substance used for separating the phosphoric acid. The proposed method gave unsatisfactory results with the presence of peroxide of iron and alumina. When iron alone is present, it requires but a slight modification; but with the presence of alumina the difficulties increase to such an extent that the method becomes inapplicable.

It is however often of importance to be able to determine the

* Chem. Gaz., vol. vii. pp. 177, 199.

phosphoric acid with accuracy in complex compounds which also contain alumina. In several rocks, especially in the basalts, salts of phosphoric acid occur, principally apatite; and undoubtedly the great fertility of a soil consisting of decomposed basalt is owing to the admixture of apatite.

When basalt is treated in the pulverized state with a dilute acid, this dissolves the apatite, together with the constituents of the decomposed zeolitic mineral soluble in acids, among which alumina is almost always present. Now by means of the molybdate of ammonia the acid solution can easily be tested for a small quantity of phosphoric acid, in order that when present, even in minute quantity, it may not be overlooked in the analysis.

After numerous experiments, the author has found the following method to be the most advantageous for analysing quantitatively complex phosphatic compounds containing alumina. The phosphate is dissolved in an acid, nitric or hydrochloric acid; and after dilution with water, a sufficient quantity of carbonate of baryta added. After it has stood for a couple of days in the cold, having been frequently agitated, it is filtered and the insoluble residue washed with cold water. The filtered solution contains the bases which were combined with the phosphoric acid, excepting alumina, peroxide of iron, and other weak bases. These, as well as the whole amount of phosphoric acid, are thus completely precipitated. The dissolved baryta is removed from the solution by sulphuric acid. This is somewhat difficult when much lime is present. In the filtered solution the bases are determined according to the usual methods.

The insoluble residue contains the whole amount of phosphoric acid which was present in the compound, as well as the alumina and the peroxide of iron. It is dissolved in dilute hydrochloric acid, and the baryta removed by sulphuric acid. The filtered solution is saturated with carbonate of soda, and evaporated to dryness; the dry mass is mixed with silica and carbonate of soda, and heated to redness. The calcined mass is digested in water, and carbonate of ammonia added to it, when a considerable amount of silica is precipitated; it is filtered. The filtered liquid contains the whole of the phosphoric acid; it is supersaturated with hydrochloric acid, then with ammonia, and the phosphoric acid precipitated as ammonio-phosphate of magnesia.

The insoluble residue is digested with muriatic acid, and the whole evaporated to dryness. The dry mass is humected with hydrochloric acid, and the silica separated in the usual manner, after which the alumina and peroxide of iron are determined.—*Bericht der Berliner Academie,* 1849, p. 220.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Decomposition of Aniline by Nitrous Acid.

By T. S. Hunt, *of the Geological Commission of Canada.*

Although modern researches have shown that several azotized bodies, besides those formed by the direct action of ammonia, may under certain circumstances be separated into that substance and a non-azotized body, yet these have either been neutral substances or acids; and if we except urea, melamine, and some of those amides of the cyanic series, none of the alkaloids have ever yet been found susceptible of such a decomposition. They combine directly with the strongest acids, and resist the action of hydrate of potash, which often evolves new bases from them, and even from neutral substances. Piria, in his beautiful memoir on asparagine*, has however pointed out the action of nitric acid containing nitrous acid as a means of effecting this decomposition in bodies which, like that substance, had hitherto resisted all agents; and he has shown, moreover, that benzamide and butyramide are easily decomposed with the liberation of their respective acids, when a current of nitric oxide gas is passed through their solutions in nitric acid.

Led by these considerations, I was desirous of submitting to the action of nitrous acid some of the organic alkaloids, and I selected aniline as the one most convenient for the purpose. Hofmann has shown that the compound of ammonia and phenole is slowly converted into this alkaloid, with the elimination of water, when exposed in sealed tubes to a high temperature; and it was to be expected, if this plan of research proved successful, that phenole might be regenerated. Accordingly, some pure aniline, obtained by the distillation of indigo with hydrate of potash, and carefully rectified, was dissolved in nitric acid; the saturated solution of the nitrate thus obtained was mixed with half its volume of nitric acid, spec. grav. 1·25, and 3 or 4 vols. of water. The gas evolved by the action of heated nitric acid upon mercury was then passed through the cold liquid; but no action was perceived, and the orange-red fumes of nitrous acid passed off into the air. The solution was then heated to about 170° F., and again submitted to the action of the nitric oxide; immediate absorption and a violent action ensued; the

* Ann. de Chim. et de Phys., Feb. 1848.

whole liquid effervesced from the escape of a colourless inodorous gas, which had the characters of nitrogen. The liquid, which before was transparent, grew brownish and turbid, and soon an oily film appeared on its surface. When the effervescence had ceased, and the odour of nitrous acid announced that the reaction was complete, the liquid was cooled and agitated with æther; the ætherial solution, decanted, filtered, and evaporated at a gentle heat, left an oily liquid, which was nearly equal in volume to the aniline employed.

It was brownish coloured, and possessed in the highest degree the peculiar odour of castoreum, with an acrid caustic taste. It was more dense than water, and soluble to a small extent in that liquid, to which it imparted its own smoky flavour; a splinter of pine-wood, moistened with this solution and then dipped in nitric acid, assumed on drying a characteristic blue colour, changing to a dark brown. The oil was readily soluble in a solution of caustic potash, and was precipitated unchanged from this solution by hydrochloric acid. Boiled with a solution of nitrate of silver, the salt was reduced and metallic silver precipitated. The action of strong nitric acid was violent; on boiling the mixture as long as red fumes appeared, an acid was obtained which gave with potash a salt crystallizing in bright yellow needles, very sparingly soluble in water, of an intensely bitter taste, and detonating when heated, which was evidently nitrophenisate of potash. These characteristic reactions show beyond a doubt that the product of this decomposition of aniline is nothing else than phenole or carbolic acid.

The reaction may be represented by the following equation:—

1 eq. of aniline and 1 eq. of nitrous acid yield 1 eq. phenole, 2 nitrogen and 1 water.

$$C^6 H^7 N + NHO^2 = C^6 H^6 O + N^2 + H^2O^*.$$

The same process applied to conine, $C^8 H^{15} N$, should yield a body having the composition of suberone, $C^8 H^{14} O$, and cotarnine, $C^{12} H^{13} NO^3$, would probably in like manner give phloretine, $C^{12} H^{12} O^4$, or something isomeric with it. The extension of this process to the alkaloids opens a wide field for investigation; and while it promises many new compounds, may enable us to fix with greater certainty than before the composition of some of those bodies, and thus disclose relations which will guide us in obtaining artificially many of those important substances†.

As the intervention of nitric acid is objectionable from the diffi-

* Notation of M. Gerhardt.

† An examination of the action of reducing agents upon the æther of nitrid organic acids promises to yield some interesting bodies of this class. I mixed an alcoholic solution of nitrobenzoic æther with sulphuric acid, and digested this with zinc until water no longer precipitated any æther from the solution; the alcohol being removed by evaporation at a gentle heat, caustic lime was added and the liquid agitated with æther. The ætherial solution left upon evaporation a heavy oil of a very pungent taste, which was insoluble in water, but dissolved instantly in dilute sulphuric acid; the solution gave by evaporation a white crystalline salt. The quantity of æther operated upon was very small, and I have not since been able to examine further the product, which appears to be a new alkaloid.

culty of getting rid of it afterwards, and from its tendency to change many organic substances, I thought, reasoning from the ready decomposition of nitrite of ammonia, that the formation of hyponitrites of the other alkaloids might obviate these objections and yield satisfactory results. In pursuance of this idea, having made a solution of nitrite of silver in boiling water, I added to the still hot liquid crystallized hydrochlorate of aniline in small successive portions; a precipitation of chloride of silver immediately appeared, followed after each addition by a violent effervescence, which was due to the evolution of a colourless neutral gas, without doubt nitrogen. Heat was then applied to the solution until the effervescence ceased, and the liquid, which had assumed a dark brown colour and was covered with an oily film, was treated with æther as in the previous experiment. The ætherial solution left upon evaporation a brownish, adhesive, semi-fluid substance, which had a strong odour of castoreum, gave with an acid the peculiar blue tint to pine-wood, and in all its reactions was identified with the product obtained by the action of nitric oxide upon the nitrate of aniline.

The clear watery solution which had separated from the æther contained an excess of the nitrite of silver, and gave with a hypochlorite no evidence of the presence of aniline. The brown colour and altered character of the phenole in this experiment were probably due to the action of the silver salt at a high temperature, which, like the nitrate in similar circumstances, seems to be partially reduced.

The reaction between an alkalamide and a nitrite is one which results in the production of a new saline genus in place of the nitrite and the formation of a new amide or an anhydride amide and water; for I have shown, both from the decomposition of the nitrite of ammonia and from its atomic volume, that gaseous nitrogen may be regarded as an anhydride amide, represented by NN. The proper amide of nitrous acid, $(NHO^2, NH^3) - H^2O = N^2H^2O$, is, like carbonic acid, decomposed at the moment of its liberation into an anhydride and water.

As my official duties call me immediately to the field, I am unable to follow out further these researches upon the alkaloids, but give my results, hoping that some other person may find time and inclination to pursue the investigation.—Silliman's *Journal* for Nov. 1849.

Analysis of Californian Gold. By F. Oswald.

This sample, obtained from London, consisted of small grains weighing respectively 48, 30, 24 and 18 grs., mixed with a fine ferruginous sand containing some iron spangles and a few particles of sulphuret of lead.

The gold itself had a very high colour; a fine streak, like the finest ducat gold; a dirty dull appearance, arising from brownish-red peroxide of iron, alumina, silica and calcareous sediment, which could be removed partially by digestion in sulphuric acid. The spe-

cific gravity of the pure pieces was 17·4. They consisted in 100 parts of—

			T. H. Henry found
Gold	87·6		Gold 88·75
Silver	8·7		Silver 8·88
Residue consisting of—			Copper and iron .. 0·85
Peroxide of iron	1·7	3·7	Siliceous residue .. 1·40
Alumina			
Lime	2·0		
Silica			
Moisture			
	100·0		

and a small loss.

The alloy of gold and silver which it contains consists consequently of—

		T. H. Henry obtained	
Gold	909·66	Gold	90·01
Silver	90·34	Silver	9·01
		Copper	0·86

and corresponds to an alloy of 21·48 carats. On comparing the author's analysis with that of Henry, it is evident that the Californian gold does not occur everywhere alike as regards the amount of silver; and that the accompanying constituents are not in all cases the same, but vary either with the nature of the soil, or with the greater or less care employed in the washing.—Poggendorff's *Annalen*, lxxviii. p. 96.

On the Separation of some Acids of the Series $(CH)^n O^4$. *By* Prof. J. Liebig.

In order to discover small quantities of butyric and valerianic acids in a mixture of the two, and to obtain the acids in a fit state for analysis, the following plan is most advantageous:—

A portion of the acid mixture is saturated with potash or soda, the remaining portion of acid is added to the neutralized portion, and the whole subjected to distillation. Two cases now occur; if the valerianic acid in the mixture amount to more than is sufficient to neutralize the whole of the alkali, the residue contains no butyric acid, but pure valerianic acid. If the quantity of the valerianic acid be less, a proportionate amount of butyric acid is left with the whole of the valerianic acid in the residue, but the distillate consists of pure butyric acid.

The quantity of the mixed acids which is neutralized with alkali must be measured by the amount of the valerianic acid supposed to exist in the mixture; for instance, assuming 10 per cent. of valerianic acid, then one-tenth of the mixture is neutralized; but supposing it to be a valerianic acid containing 10 per cent. of butyric acid which it is wished to separate, then nine-tenths of the acid must be neutralized.

It is readily perceived that by a single operation one of the acids is always obtained pure. Either the distillate is pure butyric acid, and then the residue consists of a mixture of valerianic and butyric acids, or the distillate contains butyric and valerianic acids at the same time, and in this case the residue contains pure valerianic acid. By continuing the same treatment of the mixed residue or of the mixed distillate, *i. e.* partial saturation and distillation, it is possible to obtain from the residue another portion of one or other of the acids pure; and finally a perfect separation is effected, such as is scarcely possible by mere distillation of the acids.

As the boiling-points of these two acids differ, it will be imagined that the soda, on combining with the least volatile of the acids, in this case the valerianic, deprives it of its volatility at the temperature at which the other boils. When, in a mixture of valerianic and butyric acids, the former is rendered fixed at the boiling-point of the butyric acid, the latter can naturally be distilled off in a pure state.

A mixture of valerianic with acetic acid, or of butyric with acetic acid, behaves in a totally different manner under the same circumstances. When such a mixture is partially neutralized with potash, and then submitted to distillation, it would be expected that acetic acid would principally pass over; such however is not the case, but the two other acids distil over, although the boiling-point of acetic acid is more than 90° lower than that of butyric acid, and more than 126° lower than that of valerianic acid. This is owing to the formation of an acid acetate, which does not appear to be decomposed by either of the other two acids.

If valerianic acid is added to a solution of neutral acetate of potash, it instantly dissolves and in large quantity; in binacetate of potash the valerianic acid floats in oily drops upon the surface, and appears not to dissolve therein to a greater extent than in water. If a solution of neutral acetate of potash, to which an excess of valerianic acid has been added, is submitted to distillation, valerianic acid passes over, and the residue contains binacetate of potash together with valerianate of potash. If valerianic acid is added to binacetate of potash and the mixture distilled, valerianic acid passes over, and the binacetate is left in the retort free from valerianic acid. Butyric acid behaves precisely like valerianic acid. When therefore butyric or valerianic acid containing acetic acid is partially saturated with potash and distilled, either the whole of the acetic acid is left as an acid salt together with butyric acid, and in this case the acid which passes over is pure and free from acetic acid; or only acetic acid is left in the residue, and in this case the distillate still contains acetic acid, which can be separated from the butyric or valerianic acid by a second similar operation.—Liebig's *Annalen*, Sept. 1849.

On the Atomic Weight of Ozone. *By* G. Osann.

Osann recently found that the black precipitate which ozonized oxygen precipitates from a solution of nitrate of silver mixed with

ammonia, consists of 97·56 per cent. of silver and 2·44 of oxygen. These experiments he has since repeated. The black precipitate was obtained by passing atmospheric air over fragments of phosphorus contained in a long glass tube, and conveying the ozonized air into an ammoniacal solution of nitrate of silver. After it had been well-washed and dried, it was reduced by hydrogen. The following are the results obtained:—

	Weight of substance employed.	After treatment with hydrogen.	Per-centage of silver.	Per-centage of ozone-oxygen.
1.	0·5772 grm.	0·5624	97·35	2·65
2.	0·4142	0·4030	97·24	2·76
3.	0·5180	0·5035	97·20	2·80

The mean from these experiments, 97·26, nearly agrees with the first result. It differs from the composition of the protoxide of silver, Ag^2O, and agrees better with the formula Ag^3O. Perhaps however the black precipitate is no oxide, but a combination with a peculiar substance, which the author designates for the present with the name of *ozone-oxygen*. The composition of the oxide of lead precipitate recently described* by the author, and which was obtained by passing ozonized oxygen through a solution of oxide of lead in potash, speaks likewise in favour of the above view. The author found, on analysing that precipitate, 94·85 per cent. of lead, whilst the composition of the oxide of lead (PbO) requires 92·86 per cent. Now if ozone-oxygen is a distinct body, it must have a separate atomic weight; this induced the author to calculate the atomic weight from the composition of the lead and silver compounds. With the lead compound we obtain—

$$\frac{5{\cdot}15 \times 103{\cdot}738}{94{\cdot}85} = 5{\cdot}63;$$

and if calculated from the composition of the silver compound, we obtain, assuming it to contain 2 atoms of silver—

$$\frac{2{\cdot}74 \times 2 \,.\, 108{\cdot}146}{97{\cdot}26} = 6{\cdot}10.$$

These numbers do not agree so well as we have a right to expect in determinations of the atomic weight; however the determinations were not made for this purpose. They appear for the present to prove that ozone-oxygen has a definite atomic weight; that it is by no means a modification of oxygen, but a peculiar substance like chlorine, bromine, &c.; but whether of a simple or compound nature cannot be stated. If it be admitted that ozone-oxygen is a distinct body, this will explain in a most simple manner how oxide of lead is precipitated from its solution in potash, and a precipitate of silver is obtained from the solution of nitrate of silver in ammonia. —Poggendorff's *Annalen*, lxxviii. p. 98.

* See page 15 of the present volume.

Analyses of Artificial Graphite. *By* F. C. Wrightson, Esq.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Laboratory, Temple Buildings, Birmingham,
January 5th, 1850.

Dear Sir,—You will oblige me by inserting in your next Number the following analyses of the artificial graphite obtained in the analysis of the cast irons as indicated, and which were accidentally omitted to be sent along with the rest of the analyses.

I remain, yours faithfully,
F. C. Wrightson.

Analysis of Compound separated from the Irons C. I., C. III. *and* H. VIII. *by Hydrochloric Acid.*

C. I.		C. III.	
Carbon	32·36	Carbon	34·51
Silica	40·00	Silica	22·19
Peroxide of iron	19·00	Peroxide of iron	37·50
Traces of alumina, lime, &c.		Traces of lime, &c.	
Water and loss	8·64	Water	4·70
	100·00		98·90

H. VIII.	
Carbon	11·76
Iron	79·52
Silica, with small quantities of oxide of iron, lime and alumina	9·48
	100·76

The carbon was determined by combustion with chromate of lead; the silica, &c. by fusion of the substance with a mixture of nitrate of potash and carbonate of soda. The 9·48 in H. VIII. was what remained on treating the fused mass with acid, evaporating to dryness, &c., and was composed as indicated. It will easily be seen, that all, or *nearly* all, the iron in C. I. and C. III. must have been in the state of peroxide, whilst that of H. VIII. must necessarily have existed in the metallic state, or rather as a carburet, with the exception of a small portion contained as a silicate. $Fe^3 C^2$ would require 73·00 iron for 11·76 carbon. When this substance was ignited for more than an hour over an Argand lamp, it was apparently little altered, and was nearly the same in weight.

On the Removal of Sulphuretted Hydrogen from Solutions in Quantitative Analysis. *By* Prof. H. Rose.

In the quantitative determination of chlorine, it is very frequently requisite to precipitate the metals combined with it by sulphuretted hydrogen. When the hydrochloric acid contained in the liquid filtered from metallic sulphurets is precipitated by a solution of nitrate of silver, a mixture of chloride and sulphuret of silver is obtained. It is not advisable to remove the sulphuretted hydrogen by heating

the liquid, as some hydrochloric acid might also be volatilized. To separate the recently precipitated chloride from the sulphuret of silver by ammonia is inconvenient, and renders the estimation of the chlorine less accurate. I formerly employed a solution of sulphate or nitrate of copper to remove the sulphuretted hydrogen as sulphuret of copper; but this occasions a loss of chlorine, as the sulphuret of copper is precipitated in combination with chloride of copper, in the state of an insoluble compound. But the same is also the case when solutions of other metallic oxides which can be separated as sulphurets from acid solutions by sulphuretted hydrogen, or even when the hydrates of these oxides are used. In this case, there are formed, when an excess of the salt of the metallic oxide comes in contact with sulphuretted hydrogen, similar compounds of sulphuret with the chloride or with a salt of the metallic oxide, as have long been known in the case of mercury, only these compounds do not differ in colour so much from the sulphurets as is the case with the mercurial compounds.

The best plan of destroying and removing the sulphuretted hydrogen in solution, without the danger of incurring a loss of chlorine, is by a solution of the persulphate of iron, which can be kept ready for this purpose; by its addition only sulphur is precipitated, which contains no chlorine and can be separated by filtration. The chlorine is then precipitated by nitrate of silver as chloride.—Poggendorff's *Annalen*, Dec. 7, 1849.

On some Salts of Phosphoric Acid. *By* O. B. Kuhn.

Baryta Salt, $2BaO, HO + PO^5$, is the precipitate obtained by throwing down chloride of barium with *c*-phosphate of soda. 100 parts chloride of barium furnished 96·7 parts of a precipitate dried in the air. At 266° it lost 0·36; at 428°, 0·54; and on ignition, 3·79 per cent. of water. The air-dried precipitate consists therefore of—

Baryta	64·83	2	= 153·2	65·41
Phosphoric acid ..	31·38	1	72·0	30·75
Water	3·79	1	9·0	3·84

In an experiment repeated by M. Schutz, 100 parts of chloride of barium furnished with *c*-phosphate of soda 96·4 parts of a precipitate, which on ignition lost 0·48 per cent. With the exception of some adherent water, this result agrees with the previous one; the same quantity of baryta was found in the precipitate by decomposition with sulphuric acid.

Baryta Salt, $3BaO + 2PO^5$, was obtained on dissolving the preceding precipitate after calcination in muriatic acid and precipitating with ammonia. It furnished 72·42 per cent. of baryta, or $2\frac{1}{2}$ atoms to 1 atom of phosphoric acid. Recently-precipitated phosphate of baryta, of the above composition, was digested with ammonia. The calcined salt furnished 72·63 and 72·03 per cent. baryta.

Salt of Strontia, $2SrO, HO + PO^5$, prepared like the first salt of

baryta, lost at about 248° 2·20 per cent. water, and the residue on calcination 4·39 per cent. It contains 56·02 per cent. of strontia; the above formula requires 56·12 per cent. and 4·88 per cent. of water.

Strontia Salt, $3SrO, PO^5 + 3(2SrO, HO, PO^5) + 16HO$, was obtained only once on partially precipitating chloride of strontium in the cold by *c*-phosphate of soda. The precipitate lost on ignition 18·78 per cent. water, and contained 50·24 per cent. strontia; theory requires 50·49 and 18·44 water.

A salt of the same composition as the preceding one, but containing only 4 atoms of water, was obtained on precipitating chloride of strontium with *c*-phosphate of soda and ammonia. The precipitate lost on ignition 11·41 per cent., and gave 56·47 strontia.

Lime Salt, a light flocculent phosphate, of four different preparations, gave results intermediate between $2CaO, 4HO + PO^5$ and $2CaO, 5HO + PO^5$:—

Lime	32·96	33·05	34·37	36·19
Water	25·49	25·45	23·89	21·88
Phosphoric acid	41·55	41·50	42·74	41·93

Lime Salt, a gelatinous phosphate, contained after ignition 51·36 per cent. of lime; before ignition, 11·23 per cent. of water and 45·11 per cent. of lime. It has therefore the following formula:—

$$2(3CaO + PO^5) + (2CaO, HO + PO^5) + 5HO.$$

Phosphate of Lime, dissolved in phosphoric acid and mixed with alcohol, gave a precipitate which dissolved entirely in water. Heated in an air-bath, a portion which had been dried in the air lost at 284° 27·48 per cent. in twenty-four hours; at 356°, 0·78; and on ignition, 11·97. The residue resembled enamel, was full of vesicles, and did not dissolve entirely in nitric acid after long boiling. The insoluble portion formed about the half, and was crystallized in microscopic needles. Some of the salt, which had been kept for a long time over sulphuric acid, lost, on being heated up to 340°, 19·82; at 419°, 10·29; and on calcination, 8·45; altogether, therefore, 38·56 per cent. of water. Analysis gave—

Lime	24·48	24·29	24·81	5 = 140		24·48
Phosphoric acid	39·70	38·51	38·80	3	216	37·76
Water	38·56	..	38·00	24	216	37·76
	102·74		101·61		572	100·00

If, as asserted by Berzelius, the analysed salt $= 4CaO + 3PO^5$, then 27·4 HO should have been found for 24·5 CaO and 48·1 PO^5.

The salt so prepared is only a mixture. A second preparation furnished a salt of the same composition, but in a third it was totally different. The sample from the second preparation was not calcined, but exhausted with cold water, and the soluble and insoluble portions analysed separately. It resulted from this that the phosphoric acid in the soluble portion was to the lime in the ratio of $72 : 45·8$ or $3 \times 72 : 137·4$; with 3 atoms of phosphoric acid there are therefore not quite 5 atoms of CaO. In the insoluble part the

proportion is 72 : 56, or exactly $2CaO+PO^5$; altogether the relation is 72 : 47·1 = 3 × 72 : 141·2. The water amounts to 28 atoms for $5CaO+5PO^5$. The formula therefore is $2(2CaO, HO+PO^5)+(CaO, 2HO+PO^5)+20$ to 24HO. Analysis furnished 23·23 per cent. of lime, 35·52 phosphoric acid, and consequently 41·25 water.

On again precipitating phosphate of lime dissolved in phosphoric acid with alcohol, the phosphoric acid this time being perfectly saturated with phosphate of lime, a perfectly crystalline precipitate resulted, two-thirds of which dissolved in water. The analysis of this product gave—

Lime	20·37	1 =	28	25·05
Phosphoric acid	57·00	1	72	56·69
Water	33·20	3	27	21·26

The lime salts, precipitated by alcohol as above directed, are very readily decomposed by water and by alcohol. The lime salt described by Berzelius as $4CaO+PO^5$ is likewise a product of decomposition.

Salts of Magnesia.—A cold solution of sulphate of magnesia was precipitated by a cold saturated solution of *c*-phosphate of soda.

The crystalline pulverulent precipitate, after being dried in the air, furnished on ignition 53·06 water, and contained 17·9 per cent. magnesia. Another salt, prepared in the same manner, but washed with hot water, and which had been kept in a warm place for some time in a covered watch-glass, and then left at the ordinary temperature exposed to the air, gave 13·16 per cent. loss by ignition; and—

Magnesia	34·70	12 =	240	34·80
Phosphoric acid	52·68	5	360	52·16
Water	13·16	10	90	13·04

According to this analysis the formula of the salt would be

$$2(3MgO+3PO^5)+3(2MgO, HO+PO^5)+7HO.$$

On precipitating a boiling hot solution of sulphate of magnesia with a boiling-hot solution of *c*-phosphate of soda, which had been saturated in the cold, a precipitate was obtained, which in the air-dried state experienced on ignition a loss of 23·11 per cent. It gave—

Magnesia	31·54	5 =	100	31·65
Phosphoric acid	loss	2	144	45·57
Water	23·11	8	72	22·78

A precipitate, obtained in the same manner, furnished on analysis, after being dried—

Magnesia	23·40	$2\frac{1}{2}$ =	50·0	24·20
Phosphoric acid	34·76	1	72·0	34·70
Loss	41·84	$9\frac{1}{2}$	85·5	41·10

The two formulæ which correspond to these values are

$$(3MgO+PO^5)+(2MgO, HO+PO^5)+7 \text{ and } 18HO.$$

On precipitating sulphate of magnesia with *c*-phosphate of soda,

the effloresced crystalline pulverulent precipitate, which was not perfectly free from sulphate, varied in composition between $7MgO + 4PO^5$ and $8MgO + 5PO^5$.

When phosphate of magnesia was dissolved in ordinary phosphoric acid and the liquid mixed with alcohol, a heavy oily liquid was produced, which has remained clear for nearly ten years beneath the alcohol. A portion of this liquid was analysed, the water and phosphoric acid being determined. There was found—

Magnesia	loss	4	= 80	12·54
Phosphoric acid	33·84	3	216	33·85
Water	54·27	38	342	53·61

The resulting formula is

$$2(MgO, HO + PO^5) + 2(MgO, 2HO + PO^5) + 33HO.$$

[To be continued.]

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

New Process for extracting Sugar from the Sugar-Cane. By M. Melsens.

The following account of the new and important method of extracting sugar from the sugar-cane, is abridged from the first of two long articles recently published in the *Courier de l'Europe*.

The great difficulty which has been experienced up to the present time in the preparation of sugar, has been owing to the rapidity with which it, when dissolved in water, alters by exposure to the air in hot climates. It must, however, be clear, since the cells of the sugar-cane are themselves full of sugar dissolved in water, and this solution can be kept for a long time in them, without undergoing any alteration at all, that if the same conditions which exist in nature could only be obtained in practice, there is no reason why an artificial solution of sugar may not be kept unaltered for a considerable space of time; or in other words, why water should not be used for the purpose of dissolving the sugar out of the crude juice expressed from the cane.

The difficulties, indeed, are not owing to the sugar or to the water, but to the air, and the ferments produced by its action on the crude sap of the sugar-cane. The object of M. Melsens was, then, to exclude the air from the sap when extracted from the cane, and to prevent the formation of any ferments which might change the character of the saccharine matter. This he has succeeded in doing by availing himself of the well-known affinity of sulphurous acid for oxygen gas. Sulphurous acid, however, alone was found not to answer the purpose; the sulphuric acid, produced by the absorption

of oxygen by sulphurous acid, acting on the sugar, converts it into grape-sugar. This difficulty has been overcome by using sulphurous acid combined with a powerful base, which, as the sulphurous acid is converted into sulphuric acid, combines with the latter and forms an insoluble salt.

The acid sulphites, and more especially the bisulphite of lime, were employed by M. Melsens for the double purpose of preventing fermentation by the action of the sulphurous acid, and of neutralising the sulphuric acid as fast as it formed by means of the lime.

Sugar-candy dissolved in cold water containing bisulphite of lime, even in excess, crystallized entirely, and without undergoing any change, by spontaneous evaporation, at a low temperature. Several other experiments of the same nature, but differing in their details, always gave the same result; in each the sugar crystallized out by spontaneous evaporation, without any loss either in quantity or in quality, and without any appearance of molasses. In these experiments, the sugar dissolved in water, containing bisulphite of lime in excess, was boiled, and then left to evaporate, sometimes after being filtered, sometimes without any filtration at all.

From the experiments which M. Melsens has made with bisulphite of lime, it is probable that if a cold solution of this salt were to be poured on the sugar-cane grinder, so as to mix with the juice the moment it is expressed from the cane, the sugar might be kept for some time, and might be exposed to the heat necessary for its clarification without any sensible loss or deterioration.

But this same salt also possesses the property of coagulating, at a temperature of 212°, milk, white of egg, blood, and yolk of egg mixed with water. At a temperature of 212°, bisulphite of lime acts as a clarifier. It separates the albumen, caseum, and other similar azotized matters which are found in the sugar-cane. This separation is effected without appreciable loss in the quantity, or deterioration in the quality, of the sugar.

Bisulphite of lime, moreover, rapidly and tolerably effectually bleaches the coloured substances found in the sugar-cane; it prevents the formation of other coloured matters produced by the action of air on the pulp of the cane; it also stops the production of those which are formed during evaporation, and above all of those which require for their development the joint action of air and a free alkali.

It seems that coloured substances, which, under ordinary circumstances, are formed spontaneously by the exposure of the pulp of the sugar-cane to the air, never make their appearance when bisulphite of lime is employed. By evaporating, at a low temperature, bisulphite of lime mixed with—1, a common solution of sugar; 2, the crude sap of the sugar-cane; 3, the juice of beet-root; no coloration was produced. By an evaporation of the same substances at a high temperature, the coloration was scarcely visible; indeed, with red beet-root the colour was completely destroyed, and the sugar obtained was perfectly white.

It seems, then, that bisulphite of lime can be employed in the

extraction of sugar :—1st, as an antiseptic, preventing the production and action of any ferment; 2nd, as a substance greedy of oxygen, opposing any alteration that might be caused by its action on the juice; 3rd, as a clarifier, coagulating at a temperature of 212° all albuminous and other coagulable matters; 4th, as a body bleaching all pre-existing coloured products; 5th, as a body opposing itself in a very high degree to the formation of coloured substances; 6th, as a base capable of neutralising any hurtful acids which might exist or be formed in the juice, and substituting in their place a weak inactive acid, namely, sulphurous acid.

M. Melsens is of opinion that sugar can be obtained from the sugar-cane with no other source of heat than a tropical sun, excepting only for the purpose of clarification; indeed, the bisulphite of lime prevents the crude juice of the cane, or the syrup obtained therefrom, from undergoing any changes; great rapidity in the process of crystallization, indispensable at present, becomes by using this salt unnecessary; and more than this, the quantity of sugar which is now lost in the bagasse, in consequence of the impossibility of washing it out unchanged, can be all collected by being dissolved in water charged with bisulphite of lime.

The only objection that can be made to the above process is, that the sugar obtained by means of bisulphite of lime has a sulphurous taste; this is true, but the taste is completely lost—1st, by crushing the sugar and exposing it to the air, whereby the little sulphite of lime which there may be is converted into a tasteless sulphate; 2nd, by exposing the sugar to an atmosphere containing ammonia; if this is done the sugar acquires a very agreeable flavour of vanilla, but is apt to become a little discoloured; 3rd, by clarifying it until it loses 10 per cent. of its weight; by this process a pure white sugar can be obtained, which will bear comparison with any sample produced at present. The last is the process recommended to be used on a large scale. The quantity of sugar fit for the market which can be obtained from the sugar-cane by adopting bisulphite of lime, as above recommended, is at least double that obtained by the usual processes.

In consequence of M. Melsens having made all his experiments on the sugar-cane at Paris, and therefore on a small scale, he is not able to state how bisulphite of lime can best be used in the large colonial sugar manufactories, but is compelled to leave the application of the principles on which his method depends to the intelligence of the manufacturers themselves.

In the preparation of beet-root sugar bisulphite of lime is quite as useful as in the extraction of cane-sugar; the way in which it is to be employed in the former is fully explained in the second article published in the 507th number of the *Courier de l'Europe*, to which we must refer those among our readers who desire any further information on the subject.—*Gard. Chron., Dec.* 15, 1849.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 21, 1849.

"On the Nitroprussides, a new Class of Salts." By Dr. Lyon Playfair, F.R.S., F.C.S.

When nitric acid is made to act on yellow prusside of potassium, in the proportion of one equivalent of acid for every equivalent of potassium present in the salt, the following reactions are observed. The salt dissolves in the acid with a dark red, almost black colour, a very little nitric oxide is evolved, which soon ceases, and is followed by a copious evolution of cyanogen mixed with nitrogen. The continued action of the acid causes the liquid to lose the usual reactions of red prusside of potassium; the addition of sulphate of iron now produces a slate-coloured instead of blue precipitate. On allowing the solution to cool, abundance of nitrate of potash crystallizes out, mixed with a little prussian blue, and about 5 per cent. of the original weight of the salt, of a white granular substance, which is scarcely soluble in cold, and only very slightly so in boiling water. This white substance, on examination, proves to be the remarkable body *oxamide*, the production of which in an oxidising medium is highly singular.

The dark red supernatant liquor, being neutralized with an alkaline carbonate, and boiled, deposits a green precipitate and yields a clear ruby-red solution. This solution furnishes the new class of salts, which is the subject of this paper. It may be evaporated to crystallization, and yields the nitroprusside of the base used in the neutralization.

The characters of the nitroprussides thus obtained are very marked, and cannot be confounded with those of any known class of salts.

With soluble sulphurets, the nitroprussides produce the most magnificent purple-coloured solution, and of such intensity, that they form by far the best test for the presence of a sulphuret, and betray its presence when the usual tests for a sulphuret are insufficient to expose it.

With a protosulphate of iron, the nitroprussides produce a salmon-coloured precipitate; with salts of silver, zinc and cobalt, a precipitate of a flesh colour; and with nickel, a dirty white precipitate. With a salt of copper, the precipitate is of a light green, and with salts of lead, no precipitate is occasioned.

Nitroprussic acid is obtained by adding muriatic acid to the silver salt, and forms a dark red solution, which yields on evaporation *in vacuo*, large and well-defined crystals.

The nitroprussides of sodium, potassium, ammonium, barium and calcium, are all soluble and crystallize readily, forming fine large red crystals, which have been measured by Prof. Miller of Cambridge, and are described in the paper. The salts of barium and calcium decompose on evaporation, and can after that no longer be

obtained perfectly pure, having dissolved about one per cent. of the products of decomposition, which are not removed by subsequent crystallization.

Potash and soda in the cold unite with the nitroprussides, and form distinct salts, in which there is one equivalent of these alkalies for every equivalent of the nitroprusside. These alkalies when heated with the nitroprussides decompose them altogether, forming peroxide of iron, hyponitrites, oxalic acid and ordinary ferrocyanides.

Sulphuretted hydrogen and soluble sulphurets also decompose the nitroprussides.

The formula of the nitroprussides is remarkably complex. Well-accordant analyses of all the salts permit no simpler relation between their carbon and iron than 24 equivs. of the former to 5 equivs. of the latter. The simpler proportion of 25 to 5 or 5 to 1, cannot be drawn legitimately from their composition. Analysis, and also a study of their transformation, show that they contain nitrous oxide, and have led to the complex formula

$$Fe_5Cy_{12}3NO+5R.$$

This is obviously a conjugate formula, and allows itself to be divided, for reasons now to be given, into the more simple expression

$$2(Fe_2Cy_3NO+2R)+(FeCy_2NO+R).$$

The relation of nitroprussides to ordinary prussides is supposed to be as follows:—

Both the ferrocyanides and the ferridcyanides are supposed to contain a common radical, one being quadribasic and the other tribasic, just as in the case of the modifications of phosphoric acid. A bibasic modification is therefore to be looked for. The formulæ would be as follows:

Ferrocyanides	$(Fe_2Cy_6)+4R.$
Ferridcyanides.....	$(Fe_2Cy_6)+3R.$
Hypothetical compound ..	$(Fe_2Cy_6)+2R.$

The nitroprussides are supposed to correspond to the last of the series, in which one equivalent of cyanogen is replaced by one equiv. of nitrous oxide. In the case of the beautiful purple compound produced by the soluble sulphurets on nitroprussides, this nitrous oxide is replaced by sulphuret of nitrogen. The hypothetical bibasic prusside necessary to establish this view has not yet been obtained; but the author states that experiments made with this view have already been so successful, that he shortly expects to announce it to the Society.

"On the Motion of Gases."—Part II. By Thomas Graham, F.R.S. &c.

The experiments of the former paper by the author on the same subject, afforded grounds for assuming the existence of a relation in the transpirability of different gases, that is, their passage through capillary tubes of an equally simple nature as that which is recognized among the specific gravities of gases, or even as the still more mple ratios of their combining volumes. Compared with solids

and liquids, matter in the form of gas is susceptible of small variation in physical properties, and exhibits only a few grand features. These differences of property, which are preserved amidst the prevailing uniformity of gases, may well be supposed to be among the most deep-seated and fundamental in their nature with which matter is endowed. Under such impressions he has devoted an unusual amount of time and attention to the determination of this class of numerical constants. As the results, too, were entirely novel, and wholly unprovided for in the received view of the gaseous constitution, of which indeed they prove the incompleteness, it was the more necessary to verify every fact with the greatest care.

The most general and simple of the results is, that the transpiration velocity of hydrogen gas is exactly double that of nitrogen gas. These gases, it will be remembered, have a less simple relation in density, namely 1 to 14. This was the conclusion respecting the transpiration of these gases of his former paper, and he has obtained since much new evidence in its favour. The transpirability of carbonic oxide, like the specific gravity of that gas, appears also to be identical with that of nitrogen.

The result which may be placed next in point of accuracy and importance is, that the transpiration velocity of oxygen is related to that of nitrogen in the inverse ratio of the densities of these gases, that is, as 14 to 16. In equal times it is not equal volumes but equal weights of these two gases that are transpired, the more heavy gas being more slowly transpired in proportion to its greater density. Mixtures of oxygen and nitrogen have the mean velocity of these two gases, and hence the time of air is also found to be proportional to its density when compared with the time of oxygen.

The relation between nitrogen and oxygen is equally precise as that between nitrogen and hydrogen. The densities calculated from the atomic weights of oxygen and nitrogen, namely, 16 and 14, being 1 for oxygen, 0·9010 for air and 0·8750 for nitrogen, the observed times of transpiration of equal volumes of the same gases are for oxygen 1, air 0·8970 to 0·9010, and for nitrogen 0·8708. The result for carbonic acid, which is perhaps next in interest, appears at first anomalous. It is, that the transpiration time of this gas is inversely proportional to its density when compared with oxygen, or 0·7272, the time of oxygen being 1, their velocities will of course be directly as their densities. It is to be remembered, however, that carbonic acid is a compound gas, containing an equal volume of oxygen. The second constituent, carbon, which increases the weight of the gas, appears to give additional velocity to the oxygen in the same manner and to the same extent as increased density from pressure or from cold increases the transpiration velocity of pure oxygen itself. A result of this kind shows at once the important chemical bearing of gaseous transpirability, and claims for it a place with the doctrines of gaseous densities and combining volumes. The circumstance that the transpiration time of hydrogen is one-half of that of nitrogen, indicates that the relations of transpirability are even more simple in their expression than the relations of density among gases.

In support of the same assertion may be adduced the additional fact, that binoxide of nitrogen, although differing in density, has the same transpiration time as nitrogen. Protoxide of nitrogen and carbonic acid have one transpiration time; so have nitrogen and carbonic oxide, as each pair has a common density.

The transpiration of twenty other gases and vapours is experimentally determined, and shown to be uniform, like the preceding gases, with tube resistances varying in amount from 1 to 1000. This list includes protocarburetted hydrogen, olefiant gas, ammonia, cyanogen, hydrocyanic acid, hydrosulphuric acid, bisulphide of carbon, sulphurous acid, sulphuric acid, chlorine, bromine, hydrochloric acid, ether, methylic ether, chloride of methyle, coal-gas and the vapours of water, alcohol and coal-tar naphtha.

The principal results respecting the transpiration of these vapours, and on the influence which pressure and temperature have upon the transpiration of a gas, are summed up as follows:—

The velocity of protocarburetted hydrogen is 0·8, that of hydrogen being 1.

The velocity of chlorine appears to be $1\frac{1}{2}$ that of oxygen; of bromine vapour and sulphuric acid vapour the same as that of oxygen.

Ether vapour appears to have the same velocity as hydrogen gas; their densities are as 37 to 1.

Olefiant gas, ammonia and cyanogen appear to have equal or nearly equal velocities, which approach closely to double the velocity of oxygen.

Hydrosulphuric acid gas and bisulphide of carbon vapour appear to have equal or nearly equal velocities.

The compounds of methyle appear to have a less velocity than the corresponding compounds of ethyle, but to be connected by a certain constant relation.

The resistance of a capillary tube of uniform bore to the passage of any gas is directly proportional to the length of the tube.

The velocity of passage of equal volumes of air of the same temperature, but of different densities of elasticities, is directly proportional to the density. The denser the air, the more rapidly does it pass under a constant propulsive pressure.

Rarefaction by heat has a similar and precisely equal effect in diminishing the velocity of the transpiration of equal volumes of air, as the loss of density and elasticity by diminished pressure has.

A greater resistance in the capillary is required to bring out the law of densities, than appears necessary for the two preceding results; and a resistance still further increased, and the highest of all, to bring out the law of temperatures.

Finally, transpiration is generally promoted by density, and equally whether the increased density is due to compression, to cold, or to the addition of an element in combination, as the velocity of oxygen is increased, by combining it with carbon without change of volume, in carbonic acid gas.

It did not enter into the plan of the author to investigate the passage of gases through tubes of great diameter, and to solve pneuma-

tic problems of actual occurrence, such as those offered in the distribution of coal-gas by pipes. But he states that the results must be similar, with truly elastic gases such as air and carburetted hydrogen, whether the tubes are capillary or several inches in diameter, provided the length of the tube is not less than 4000 times its diameter, as in the long glass capillaries of his experiments. The small propulsive pressure applied to coal-gas is also favourable to transpiration, as well as the great length of the mains; and he therefore would expect the distribution of coal-gas in cities to exemplify approximately the laws of gaseous transpiration. The velocity of coal-gas should be 1·575, that of air being 1, under the same pressure. And with a constant propulsive pressure in the gasometer, the flow of gas should increase in volume with a rise of the barometer or with a fall in temperature, directly in proportion to the increase of its density from either of these causes.

These laws, it will be observed, are entirely different from those which direct the passage of gases through an aperture in a thin plate, or their flow into a vacuum as it is usually said, and could not be deduced, like the latter, from our speculative ideas respecting the elastic fluids.

December 21, 1849.

The Bakerian Lecture was delivered by Professor Graham, F.R.S., "On the Diffusion of Liquids."

The apparatus used in studying the diffusion of salts and other substances into water was very simple. It consisted of an open phial to contain the solution of the salt to be diffused, which was entirely immersed in a large jar of pure water, so that the solution in the phial communicated freely with the latter. Phials cast in a mould of the capacity of four ounces of water, or more nearly 2000 grains, were generally employed, which were ground down to a uniform height of 3·8 inches. The neck was 0·5 inch in depth, and the aperture or mouth of the phial 1·25 inch in diameter. The phial was filled up with the solution to be diffused till it reached the point of a pin dipping exactly 0·5 inch into the mouth of the bottle. This being the solution cell or bottle, and the external jar the "water-jar," the pair together form a "diffusion cell." The diffusion was stopped, generally after seven or eight days, by closing the mouth of the phial with a plate of glass, and then raising it out of the water-jar. The quantity of salt which had found its way into the water-jar—the diffusion product as it was called—was then determined by evaporating to dryness.

The characters of liquid diffusion were first examined in detail with reference to common salt.

It was found, first, that with solutions containing 1, 2, 3 and 4 per cent. of salt, the quantities which diffused out of the phials into the water of the jars, and were obtained by evaporating the latter, in a constant period of eight days, were as nearly in proportion to these numbers, as 1, 1·99, 3·01 and 4·00; and that in repetitions of the experiments, the results did not vary more than 1-40th part.

The proportion of salt which diffused out in such experiments amounted to about 1-8th of the whole.

Secondly, that the proportion of salt diffused increases with the temperature; an elevation of 80° Fahr. doubling the quantity of chloride of sodium diffused in the same time.

The diffusibility of a variety of substances was next compared, a solution of 20 parts of the substance in 100 water being always used. Some of the results were as follows, the quantities diffused being expressed in grains: chloride of sodium 58·68, sulphate of magnesia 27·42, sulphate of water 69·32, crystallized cane-sugar 26·74, starch-sugar 26·94, gum-arabic 13·24, albumen 3·03. The low diffusibility of albumen is very remarkable, and the value of this property in retaining the serous fluids within the blood-vessels at once suggests itself. It was further observed, that common salt, sugar and urea, added to the albumen under diffusion, diffused away from the latter as readily as from their aqueous solutions. Urea itself is as highly diffusible as chloride of sodium.

In comparing the diffusion of salts dissolved in 10 times their weight of water, it was found that isomorphous compounds generally had an equal diffusibility, chloride of potassium corresponding with chloride of ammonium, nitrate of potash with nitrate of ammonia, and sulphate of magnesia with sulphate of zinc. The most remarkable circumstance is that these pairs are "equi-diffusive," not for chemically equivalent quantities, but for equal weights simply. The acids differed greatly in diffusibility, nitric acid being nearly four times more diffusive than phosphoric acid; but these substances also fell into groups, nitric and hydrochloric acids appearing to be equally diffusive; so also acetic and sulphuric acids. Soluble subsalts and the ammoniated salts of the metals present a surprisingly low diffusibility; the quantities diffused in similar circumstances of the three salts, sulphate of ammonia, sulphate of copper, and the blue ammonio-sulphate of copper being very nearly as 8, 4 and 1.

When two salts are mixed in the solution-cell, they diffuse out into the water atmosphere separately and independently of each other, according to their individual diffusibilities. This is quite analogous to what happens when mixed gases are diffused into air. An important consequence is, that in liquid diffusion we have a new method of separation or analysis for many soluble bodies, quite analogous in principle to the separation of unequally volatile substances in the process of distillation. Thus, it was shown that chlorides diffuse out from sulphates and carbonates, and salts of potash from salts of soda; and that from sea-water the salts of soda diffuse out into pure water faster than the salts of magnesia. The latter circumstance was applied to explain the discordant results which have been obtained by different chemists in the analyses of the water of the Dead Sea, taken near the surface; the different salts diffusing up into the sheet of fresh water, with which the lake is periodically covered, with unequal velocity.

It was further shown that chemical decompositions may be produced by liquid diffusion; the constituents of a double salt of so

much stability as common alum being separated, and the sulphate of potash diffusing in the largest proportion. In fact the diffusive force is one of great energy, and quite as capable of breaking up compounds as the unequal volatility of their constituents. Many empirical operations in the chemical arts, it was said, have their foundation in such decompositions.

Again, one salt, such as nitrate of potash, will diffuse into a solution of another salt, such as nitrate of ammonia, as rapidly as into pure water; the salts appearing mutually diffusible, as gases are known to be.

Lastly, the diffusibilities of the salts into water, like those of the gases into air, appear to be connected by simple numerical relations. These relations are best observed when dilute solutions of the salts are diffused from the solution-cell, such as 4, 2 or even 1 per cent. of salt. The quantities diffused in the same time from 4 per cent. solutions of the three salts, carbonate of potash, sulphate of potash and sulphate of ammonia, were 10·25, 10·57 and 10·51 grains respectively; and a similar approach to equality was observed in the 1, 2, and $6\frac{2}{3}$ per cent. solutions of the same salts. It also held at different temperatures. The acetate of potash appeared to coincide in diffusibility with the same group, and so did the ferrocyanide of potassium. The nitrate of potash, chlorate of potash, nitrate of ammonia, chloride of potassium and chloride of ammonium formed another equi-diffusive group. The *times* in which an equal amount of diffusion took place in these two groups appear to be as 1 for the second to 1·4142 for the first, or as 1 to the square root of 2. Now in gases, *the squares of the times* of equal diffusion are *the densities of the gases*. The relation between the sulphate of potash and nitrate of potash groups would therefore fall, to be referred to the diffusion molecule or diffusion vapour of the first group having a density represented by 2, while that of the second group is represented by 1.

The corresponding salts of soda appeared to fall into a nitrate and sulphate group also, which have the same relation to each other as the potash salts.

The relation of the salts of potash to those of soda, in times of equal diffusibility, appeared to be as the square root of 2 to the square root of 3; which gives the relation in density of their diffusion molecules, as 2 to 3. Hydrate of potash and sulphate of magnesia were less fully examined, but the first presented sensibly double the diffusibility of sulphate of potash, and four times the diffusibility of the sulphate of magnesia. If these times are all squared, the following remarkable ratios are obtained for the densities of the diffusion molecules of these different salts, each of which is the type of a class of salts, hydrate of potash 1, nitrate of potash 2, sulphate of potash 4, sulphate of magnesia 16, with nitrate of soda 3 and sulphate of soda 6.

In conclusion, it was observed, that it is these diffusion molecules of the salts which are concerned in solubility, and not the Daltonian atoms or equivalents of chemical combination; and the application was indicated of the knowledge of the diffusibilities of different substances to a proper study of endosmose.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Tannic Acid, Gallic Acid and Metagallic Acid.

By Prof. G. MULDER.

THE composition of tannic acid is generally represented by the formula $C^{18} H^5 O^9 + 3HO$. From the following investigation however it results that this acid should have the formula $C^{28} H^6 O^{17} + HO$, and that it is consequently isomeric with gallic acid.

Long ago Pelouze discovered that quercitannic acid is decomposed by heat in the same way as gallic acid. When tannic acid is exposed to a gradually increasing temperature, it loses its hygroscopic water at 248° F. From this temperature to 356° it remains unaltered, but then begins to undergo decomposition. If the temperature is raised to 482°, some acid water passes over; carbonic acid is disengaged; a sublimate, pyrogallic acid, is obtained; whilst a black substance, to which Pelouze gave the name of metagallic acid, is left in the retort.

1·254 grm. of pure tannic acid, dried at 248°, was heated in a closed test-tube, and the gas disengaged collected over mercury. The receiver contained 84 cub. centim. of air at 44°·6 F. and 762 millims. After the heating, which was continued for several hours, the gas amounted to 88 cub. centim. at 44°·6 and 761·5 millims. after the carbonic acid had been removed by potash. Besides carbonic acid, therefore, the 1·254 tannic acid had disengaged at 4·82, 4 cub. centim. of gas.

Tannic acid is not known in a perfectly pure state. According to Pelouze's method of preparation, a small quantity of a coloured substance, probably metagallic acid, remains with the tannic acid; but this cannot give rise to the 4 cub. centim. of gas, nor can it proceed from any possible admixture of gallic acid. The products of decomposition by a temperature not exceeding 482° are, according to Pelouze, water, carbonic, pyrogallic and metagallic acids. These results have been confirmed by my investigations. A quantitative determination of the four products of decomposition is connected with many difficulties. The expelled water dissolves pyrogallic acid and diminishes its amount; the pyrogallic acid further sublimes partially in the vessel in which the tannic acid is heated, and is also partially carried away with the carbonic acid. After numerous

fruitless experiments, no other plan remained than to determine carefully the amount of metagallic acid which is produced from a known weight of tannic acid.

As regards the water which escapes at 482°, it amounted to 0·324 grm. from 5·023 grms. of tannic acid dried at 248°, which corresponds to 6·5 per cent. This water had an acid reaction, and contained some pyrogallic acid in solution. In the same experiment, after complete decomposition, 2·677 grms. metagallic acid remained in the retort, which corresponds to 53 per cent. In another experiment I obtained from 6·03 grms. of dried tannic acid 3·53 metagallic acid, corresponding to 58 per cent. A large amount of pyrogallic acid was obtained, but it was impossible to determine the quantity accurately.

Pyrogallic Acid.—This acid has the properties and composition stated by Pelouze:—

Carbon	57·18	8	57·2
Hydrogen	4·77	4	4·7
Oxygen	38·03	4	38·1

Metagallic Acid.—According to Pelouze, the composition of this acid corresponds to the formula $C^{12} H^6 O^3 + HO$, which I did not confirm. I obtained the following results on analysis. I. and II. are of different preparations:—

	I.	II.	
Carbon	62·5	62·2	62·7
Hydrogen	3·3	3·5	3·2
Oxygen	34·1	34·3	34·1

It was found impossible to separate the whole of the pyrogallic acid by treatment with hot water. The substance, after being treated with hot water and dried at 392°, gave—

Carbon	64·8
Hydrogen	2·9
Oxygen	32·3

By further heating, more pyrogallic acid was separated. On this account a fresh quantity of tannic acid was heated until no further sublimate was perceptible; it yielded—C, 67·0; H, 2·3; O, 30·7. This latter substance might be considered as pure metagallic acid. When boiled with water, it parted with neither tannic nor pyrogallic acid; it dissolved almost entirely in potash, and was again precipitated by muriatic acid. These properties agree with those of Pelouze's metagallic acid.

The precipitate obtained from the potash solution by muriatic acid, after being washed and dried at 428°, yielded 66·8 C, 2·6 H, and 30·6 O.

Metagallic acid prepared in a different manner furnished, after being dried at 302°, 66·7 C, 2·8 H, 30·5 O. That this is really the composition of pure metagallic acid will be evident from the following experiment:

Gallic Acid was kept in the same manner as tannic acid at 482° for several hours; metagallic acid remained, which was not perfectly free from gallic acid. It furnished—

	I.	II.
Carbon	61·6	60·8
Hydrogen	2·4	2·4
Oxygen	36·0	36·8

By heating the metagallic acid until nothing further sublimed, solution in potash, precipitation by muriatic acid, washing and drying at 284°, an acid was obtained from gallic acid which had precisely the same composition as that procured from tannic acid:—

	From gallic acid.	From tannic acid.				
		Impure.	Purified.		Equivs.	Theory.
Carbon	66·0	67·0	66·8	66·7	40	66·3
Hydrogen ..	2·7	2·3	2·6	2·8	10	2·8
Oxygen	31·3	30·7	30·6	30·5	14	30·9

To determine the atomic weight of metagallic acid, that prepared from tannic acid was employed. It was extremely difficult to prepare a salt of constant composition. The acid was dissolved in ammonia, excess of neutral nitrate of silver added, and the solution carefully precipitated with acetic acid. The precipitate, dried at 284°, contained ammonia and oxide of silver, had a silvery lustre, and was consequently not examined. Another portion of metagallic acid was digested with hot potash; an excess of acid was used; after several hours' digestion, the dark liquid was filtered, evaporated, and the residue dried at 266°. It gave on combustion with chromate of lead—

Carbon	58·6	40 =	3004·80	58·7
Hydrogen	2·4	10	124·80	2·4
Oxygen	26·8	14	1400·00	27·4
Potash	12·2	1	588·90	11·5

From the above experiments the following conclusions may be drawn:—1st, the statement of Pelouze, that metagallic acid obtained from tannic acid is identical with that from gallic acid, is perfectly correct; 2nd, the composition of metagallic acid is $C^{40}\,H^{10}\,O^{14}$, and not as stated by Pelouze.

The composition of metagallic acid being established, the question now arises, in what manner this acid originates from gallic and tannic acids. Both acids can be treated of at the same time, for—

Gallic acid.....	$C^{7}\,H^{5}\,O^{5} \times 4 = C^{28}\,H^{12}\,O^{20}$
And tannic acid ..	$= C^{28}\,H^{10}\,O^{18}$
	$H^{2}\,O^{2}$

Gallic acid may be simply decomposed into pyrogallic and carbonic acids, for—

2 equivs, gallic acid	$C^{14} H^{6} O^{10}$
Pyrogallic acid	$C^{12} H^{6} O^{6}$
Carbonic acid	$C^{2} O^{4}$
	$C^{14} H^{6} O^{10}$

If the temperature is raised too high in the decomposition, metagallic acid is formed:—

2 equivs. tannic acid.....	$C^{56} H^{20} O^{36}$	
Metagallic acid	$C^{40} H^{10} O^{14}$	56 per cent.
Carbonic acid	$C^{6} O^{12}$	20
Pyrogallic acid	$C^{10} H^{5} O^{5}$	17
Water	$H^{5} O^{5}$	7
	$C^{56} H^{20} O^{36}$	100

Metagallic acid stands in the following relation to the humic acids:—

Ulmic acid..... =	$C^{40} H^{14} O^{12}$
Humic acid	$C^{40} H^{12} O^{12}$
Geic acid	$C^{40} H^{12} O^{14}$
Metagallic acid.....	$C^{40} H^{10} O^{14}$

Tannic Acid, Gallic Acid, Ellagic Acid, Sugar.—It is well known that tannic acid is converted into gallic acid by long contact with oxygen; at the same time there is always a certain amount of ellagic acid formed. According to Erdmann, the latter acid is produced in large quantity along with gallic acid when nut-galls are fermented. Pelouze observes, that in this decomposition of the tannic acid there is precisely the same amount of carbonic acid disengaged as there is absorbed of oxygen. Braconnot noticed the production of alcohol in the fermentation of nut-galls. This alcohol cannot be ascribed to the presence of any sugar in the tannic acid; for tannic acid, when heated to 482°, gives no empyreumatic products, while sugar is decomposed already at 428°. Peltier found that gum with gallic acid precipitated gelatine. This observation is perfectly correct, but the precipitate is less coherent than that produced by tannic acid. Moreover, there are several substances, as for instance the so-called artificial tannins produced by the action of nitric acid, which precipitate gelatine; we must therefore abandon the notion that tannic acid consists of gallic acid and gum. Moreover, gum is decomposed at 356° into empyreumatic products.

Action of Acids upon Tannic Acid.—At the ordinary temperature, sulphuric, hydrochloric, and some other acids, precipitate tannic acid from its solutions. This precipitate is redissolved by heat; and after long digestion at a boiling temperature, it is found that a large quantity of gallic acid crystallizes on cooling, whilst there is no longer any tannic acid present in the liquid. In this metamorphosis a brown substance separates, whence several chemists have concluded that the gallic acid is contained ready-formed in the tannic acid; but there is not one single reason for this assumption; for if a weighed quantity of dry tannic acid is digested with

muriatic acid and water at 212°, preventing the access of air, but very little brown substance is formed, and the whole amount of tannic acid is converted into gallic acid. After this metamorphosis, the hydrochloric acid may be evaporated without the gallic acid experiencing any change; sulphuric acid acts in the same manner; but muriatic acid is preferable, because it can be evaporated.

Action of Alkalies upon Tannic, Gallic and Ellagic Acids.—These three substances are strongly acted upon by alkalies and decomposed; the two first give a red colour as soon as they come in contact with an excess of alkali. The red substance produced on this occasion is, according to Büchner, *tannoxylic acid*; he found its formula in the lead salt to be $C^{15} H^5 O^{11} + 3PbO$.

According to Merklein and Wöhler, ellagic acid experiences a similar change under the influence of alkalies. The solution turns blood-red, and after some time blackish-blue crystals separate, which contain *glaucomelanic acid*, $C^{12} H^2 O^6$. This acid differs from ellagic acid by $C^2 O$. If tannic acid is boiled with potash, there is formed, according to Büchner, a quantity of gallic acid closely corresponding to the amount of tannic acid employed; this gallic acid however is coloured; acids precipitate a dark-coloured substance from it, which has received the name of *tannomelanic acid*, $C^{14} H^4 O^7$.

The formation of tannoxylic acid, $C^{15} H^5 O^{11}$, from tannic acid may be explained as follows:—

2 equivs.	tannic acid	$C^{56} H^{20} O^{36}$	+ 20O from the air.
3	... tannoxylic acid ..	$C^{45} H^{15} O^{33}$	
11	... carbonic acid	C^{11} O^{22}	
5	... water	$H^{10} O^5$	
		$C^{56} H^{20} O^{60}$	

If tannomelanic acid has the composition $C^{14} H^4 O^7$, it is probably produced according to the following scheme:—

3 equivs.	tannoxylic acid ..	$C^{45} H^{15} O^{33}$	+ 22O
2	... tannomelanic acid	$C^{28} H^{10} O^{14}$	
17	... carbonic acid	C^{17} O^{34}	
7	... water	$H^{14} O^7$	
		$C^{45} H^{15} O^{55}$	

Amount of Water in Tannic Acid.—Tannic acid is a hygroscopic substance. To free it from this water, it must be kept for a long time in a current of dry air at 248°. Its formula is then $C^{28} H^9 O^{17} + HO$; mixed with oxide of lead, it lost in three experiments, 2·98, 3·04 and 2·93 per cent. of water; the above formula requires 2·8. When ammonia is passed over the hydrate of tannic acid, and the excess of ammonia is removed by a current of dry air, the compound $C^{28} H^9 O^{17}, NH^4 O + 3NH^3$ is obtained. At 212° this compound turns brown, and is then $C^{28} H^7 O^{15} + NH^4 O$; dried at 248°, it is $C^{28} H^4 O^{16}, NH^4 O$.

Equivalent of Tannic Acid.—To determine the equivalent of

tannic acid, Berzelius employed the lead salt, which he prepared by dropping neutral acetate of lead into a solution of tannic acid, and drying the precipitate at 212°. He found in this precipitate 34·21 per cent. oxide of lead, which agrees with Pelouze's analysis of the lead salt. I have obtained the following five salts of lead, which were all dried at 248° :—

$$2(C^{28}\,H^{9}\,O^{17})+3PbO$$
$$C^{28}\,H^{9}\,O^{17}+2PbO$$
$$C^{28}\,H^{9}\,O^{17}+3PbO$$
$$C^{28}\,H^{9}\,O^{17}+4PbO$$
$$C^{28}\,H^{9}\,O^{17}+5PbO$$

Combinations of Tannic Acid with Gelatine, Albumen and Proteine.—Gelatine gives a compound with tannic acid, which consists of 100 parts gelatine and 134–136 tannic acid. The formula $3(C^{13}\,H^{10}\,N^{4}\,O^{3})+2(C^{28}\,H^{9}\,O^{17})$ requires 134 parts tannic acid to 100 parts of gelatine.

Albumen furnishes a similar compound, consisting of 3 equivs. albumen and 2 equivs. tannic acid.

Proteine furnishes the same compound, and also another consisting of 1 equiv. proteine and 2 equivs. tannic acid.—*Journ. für Prakt. Chem.*, vol. xlviii. p. 90.

On the Presence of Iodine in Aluminous Schists.

Some years ago M. Forchhammer brought forward an ingenious idea respecting the part which the species of Fucus take in the formation of aluminous schists. It consisted in admitting that the Fuci, after having accumulated in their substance the sulphates contained in the sea-water, converted by putrefaction after death the sulphate of potash into sulphuret of potassium; this in its turn precipitated the iron contained in the sea-water in the state of sulphuret of iron, which became mixed with the clay and other substances, some of which are organic, and owe their presence to the putrefaction of the Fuci. Chemical analysis, by demonstrating the presence of iodine in the aluminous schists, added a new and powerful argument in favour of this hypothesis, so well established by M. Forchhammer upon numerous observations. The ash of the Fuci contains, in fact, a considerable quantity of iodine, which might lead to the supposition that this substance would be also found, at all events in small quantity, in these deposits, if the Fuci really take that part in the formation of these schists which M. Forchhammer attributes to them. Now M. Genteles, who was engaged in 1846 in some researches on the manufacture of alum, has isolated iodine from the aluminous schists of Latorp in Sweden. This discovery, joined to that of M. Duflos of the presence of iodine and bromine in the coals of Silesia, will suffice to draw the attention of geologists to the confirmation which they furnish of the ideas of M. Forchhammer respecting the formation of the aluminous schists. —Svanberg's *Jahresbericht*, p. 131.

On the Action of Potash upon Caffeine. By A. Wurtz.

When caffeine is boiled with a concentrated solution of potash, it gradually dissolves, disengaging a considerable quantity of methylamine. This volatile base may be easily condensed by receiving the vapours which are liberated in a cold flask containing a small quantity of water. When saturated with hydrochloric acid, the product of distillation furnishes a salt which is soluble in hot absolute alcohol, and crystallizes on cooling in scales. This salt forms with chloride of platinum a double salt, which is soluble in hot water, and crystallizes in orange-coloured granules. On analysis it furnished—

	Found.	Calculated.
Carbon	5·2	5·0
Hydrogen	2·6	2·5
Nitrogen		
Chlorine		
Platinum	41·7	41·5

The base which is formed by the action of potash on caffeine is therefore methylamine. In a recent investigation upon caffeine, M. Rochleder has examined the action of chlorine upon this base; he found among the products of this reaction an alkaloid which he calls formyline, the composition of which he represents by the formula $C^2H^4N^*$. On comparing the analyses of the double hydrochlorate of formyline and platinum with those of the corresponding salt of methylamine, these two salts will be found to exhibit the same composition. It is probable therefore that the formula C^2H^4N, which M. Rochleder assigns to formyline, is incorrect, and that this base, represented by the formula C^2H^7N, is identical with methylamine.—*Comptes Rendus*, Jan. 7.

Influence of an Augmentation of the Saline Matter in the Food upon the Proportion of Nitrogen contained in the Perspiration and Urine. By M. Barral.

M. Barral has recently communicated to the French Academy of Sciences the results obtained on subjecting a sheep to saline food.

About 185 grms. of chloride of sodium were given daily with the food. At the same time the excretions of the animal were analysed, and their composition compared with that of the excretions before the exhibition of the salt. This treatment was several times interrupted and resumed, the excretions being examined comparatively. The most remarkable result of these analytical investigations was, that under the influence of the saline treatment the proportion of nitrogen (urea and uric acid) excreted in the urine was augmented to a considerable extent; the same increase in the nitrogen was found; and in this respect M. Barral's results agree with those of MM. Regnault and Reiset.

* See Chem. Gaz., vol. vii. p. 460.

On the Explosions of Burning Fluids. *By* E. N. Horsford, *Rumford Professor in the University at Cambridge, U.S.A.**

It has been maintained that several of the various preparations under the general denomination of *burning fluids* are, in certain conditions, explosive. It has been asserted by vendors, on the other hand, that they are not explosive. Wherein the misapprehension lies, how the numerous accidents that have occurred in the use of burning fluids are to be explained, and by what precautions the repetition of these accidents may be prevented, have been subjects of experimental inquiry.

a. The *burning fluids*, as a class, are rectified spirits of turpentine, or turpentine with an admixture of a small per-centage of highly rectified spirits of wine, or of some other inflammable body readily soluble in turpentine or alcohol. *b.* Turpentine, alcohol and æther, when fired in an open vessel, burn at the surface so long as a supply of oxygen is kept up. *c.* A slight report attends the flash of flame at the commencement of the combustion. *d.* The accidents with burning fluids have ordinarily occurred during the filling of lamps from the cans, and always in the presence of flame, from a burning lamp or other source.

In these facts (*a*, *b*, *c*, *d*) lies the explanation of the phænomena that have been observed.

It is well known that a mixture of hydrogen and oxygen, in the proportion of 2 vols. of the former to 1 of the latter, is eminently explosive; and that atmospheric air in larger measure may be substituted for oxygen with somewhat diminished explosive tendency of the mixture. An admixture of oxygen with the hydrocarbon used for city illumination is explosive. Atmospheric air may be substituted for oxygen, as in the case above, with the like effect.

The above considerations suggested the idea, that in the chamber over the burning fluid, in the flask or can from which the lamps are filled, there might be an admixture of the vapour of the burning fluid in such proportion with atmospheric air as to make it susceptible of explosion. To test the value of this suggestion, experiments were made with alcohol, æther, and a kind of burning fluid in general use:—

Experiment 1.—A current of air was directed into the upper part of a loosely-stoppered half-filled laboratory glass spirit-lamp while burning, causing thereby a mixture of alcohol, vapour and air to rush past the flame. After a moment or two the jet took fire, and was instantaneously followed by explosion. This result was uniform.

Experiment 2.—After permitting a drop of alcohol, in a large glass flask with a small neck, to evaporate for an instant, upon applying flame to the mouth, explosion resulted frequently, though not so uniformly as in Experiment 1.

Experiment 3.—Æther, similarly treated in a glass flask, yielded

* Read before the American Academy, October 1849, and communicated by the Author.

less uniform results, because probably of the greater difficulty of obtaining the proper mixture of æther and air.

Experiment 4.—A kind of *burning fluid*, in extensive use, and said by the vendors to be *not explosive*, was subjected to similar experiment, with still less frequent affirmative results. They were however sufficient to show that explosions with it are possible. Similar experiments have been made with another variety of burning fluid by Dr. Morrill Wyman of this city (Cambridge), with like results.

It is therefore established, that when the proper amounts of burning fluid, vapour and atmospheric air are mixed together, as they may be, in the upper part of a partially-filled can or receiver, and a flame is brought sufficiently near, explosion must result. If the quantity of mixed gases be large, the explosion may cause the destruction of the containing vessel; or, if that remain entire, it may drive out a portion of the fluid, which, taking fire, may cause more or less injury.

The course of safety has been pointed out by the dealers in these articles for illumination. It is, to fill the lamps (the tops of which are without special air-holes, and which screw on) in the *absence of flame*, by daylight for example; in which case no explosion can occur.

Accidents similar to those with burning fluids have taken place in the use of the so-called air-tight stoves for burning wood. After the wood has been fired, and the supply of air for some time shut off, on reopening the draft (and sometimes without, there is reason to believe) occasional explosions of great violence have occurred, attended sometimes with the partial destruction of the stove. The probable explanation is the following.

After firing the wood and shutting off the draft, destructive distillation commences. Inflammable gases issue from the wood, which mingling with air derived from the pipe or remaining still unconsumed, furnish a mixture becoming gradually more and more explosive, until at length the proper proportions having been attained, the incandescent coal or a jet of flame causes explosion.

As these accidents are not of frequent occurrence, it may be found that the probability of producing inflammable gases in the required quantity is less with some varieties of wood than with others.

On some Salts of Phosphoric Acid. *By* O. B. Kuhn.

[Continued from p. 31.]

Zinc Salt.—Crystallized sulphate of zinc, precipitated with a strong solution of *c*-phosphate of soda in excess, forms a scaly powder, which is fatty to the touch. It has the formula $(3ZnO + PO^5) + (2ZnO, HO + PO^5) + 3HO$. Analysis gave—

Oxide of zinc.....	loss	5	= 205	*53·25*
Phosphoric acid.....	37·34	2	144	37·40
Water.....	10·55	4	36	*9·35*

Phosphate of Zinc, precipitated from an alcoholic solution of chloride of zinc by *c*-phosphoric acid as an amorphous powder, was analysed by Reich. Neglecting the water, the author deduces the formula $(3ZnO+PO^5)+2(2ZnO, HO+PO^5)$. Analysis gave—

Oxide of zinc	loss	7	= 287·0	54·62
Phosphoric acid.....	41·2	3	216·0	41·11
Water	4·4	$2\frac{1}{2}$	22·5	4·27

Phosphate of the Protoxide of Manganese.—The solution of a salt of the protoxide of manganese, precipitated with *c*-phosphate of soda, gave a somewhat crystalline precipitate, the composition of which may be expressed by $(2MnO, HO+PO^5+2HO)+(3MnO+PO^5+2HO)$:—

Protoxide of manganese....	49·06	$2\frac{1}{2}$	= 90·0	48·78
Phosphoric acid	39·76	1	72·0	39·02
Water	13·60	$2\frac{1}{2}$	22·5	12·20

On precipitating a solution of the pure protochloride with *c*-phosphate of soda, a salt with the composition $2MnO, HO+PO^5+2HO$ was obtained, as shown by the following analysis:—

Protoxide of manganese	42·32	2	= 72	42·11
Phosphoric acid	42·53	1	72	42·11
Water	15·15	3	27	17·79

On precipitating a solution of the protosulphate of manganese, which had been several times crystallized, with *c*-phosphate of soda, a salt with the composition $3MnO+PO^5+7HO$ was obtained:—

Protoxide of manganese	44·68	3	= 108	44·44
Phosphoric acid.....	loss	1	72	29·63
Water.....	27·20	7	63	25·93

8·12 grms. of crystallized phosphate of soda furnished with protosulphate of manganese 4·69 grms. precipitate of a pale reddish-white colour; on ignition it lost 25·73 per cent. The equivalent of crystallized phosphate of soda being 359·6, would give 207·7 precipitate, and the latter would lose 53·5 (=6HO) on ignition. According to this there remains 82·2 for the protoxide of manganese, which makes $2\frac{1}{2}$ equivs. The proportion $7RO : 3PO^5$ was likewise once obtained for a zinc phosphate.

Iron Salt.—When a solution of the perchloride of iron is precipitated with *c*-phosphate of soda, the precipitate is $5Fe^2O^3+6PO^5$.

Copper Salt.—Sulphate of copper was added to a solution of *c*-phosphate of soda; the bluish-white precipitate had the composition $2CuO, HO+PO^5+HO$. Judging from a change in the colour, the second atom of water may be expelled at a slightly elevated temperature. Analysis gave—

Oxide of copper	47·82	2	= 80	47·06
Phosphoric acid	loss	1	72	42·35
Water	10·37	2	18	10·59

When the solution of sulphate of copper was completely precipitated with *c*-phosphate, a salt was obtained which contained 51·32

CuO, 38·31 PO^5 and 10·37 HO, and appears to have the following composition :—$2(3CuO + PO^5 + 2HO) + 3(2CuO, HO + PO^5 + HO)$.

On adding *c*-phosphate of soda to a boiling solution of sulphate of copper, a precipitate separated, in part immediately and in part on cooling. The entire precipitate contained 50·91 oxide of copper, or the same amount as in the preceding.

Mercury Salt.—Crystallized protonitrate of mercury, digested in water without any previous application of heat with *c*-phosphate of soda, led to the formula $3Hg^2O + PO^5$. The persulphate of mercury, treated in the same manner, immediately gave a salt represented by the formula $3HgO + PO^5$. Both salts, when dried in the air, were free from water.

Lead Salts.—5·00 grms. of nitrate of lead furnished, on being precipitated with *c*-phosphate of soda in the cold, 4·39 of a precipitate, and at a boiling heat, 4·06; consequently the first precipitate contains 2, the other 3 atoms of oxide of lead. *c*-phosphate of soda gave a precipitate with an excess of acetate of lead, containing $2\frac{1}{2}$ atoms of oxide of lead.

10·36 grms. of nitrate of lead dissolved in water furnished 107·86 liquid; 48·54 of it, containing 4·56 nitrate of lead, boiled with *c*-phosphate of soda, gave 3·92 dry precipitate, which lost on calcination 0·03. The water amounts very accurately to 1 atom for 3 atoms of PO^5; consequently the formula must be $(2PbO, HO + PO^5) + 2(3PbO + PO^5)$, and when calcined $(2PbO + PO^5) + 2(3PbO + PO^5)$.

59·32 of the same solution, containing 5·70 grms. of the nitrate, when mixed cold with phosphate of soda, gave 5·02 precipitate, 4·86 of which lost on calcination 0·16. This salt has the formula $PbO, NO^5 + 2(3PbO + PO^5)$.

7·11 grms. of fresh crystallized acetate of lead were precipitated with phosphate of soda; the liquid contained no lead, and had no acid reaction. The precipitate experienced no loss on ignition, and had the formula $(2PbO + PO^5) + 3(3PbO + PO^5)$.

On dissolving insoluble phosphates in nitric acid and precipitating these solutions with acetate of lead, Dr. Reich obtained a precipitate with the formula $2\frac{1}{2}PbO + PO^5$. In other cases the author obtained precipitates corresponding to the formulæ—

$$(2PbO + PO^5) + 4(PbO + PO^5)$$
$$(2PbO + PO^5) + 5(PbO + PO^5)$$
$$(2PbO + PO^5) + 6(PbO + PO^5).$$

The phosphates of lead hitherto obtained form the following series :—$(2PbO + PO^5) + 1, 2, 3, 4, 5, 6\ (3PbO + PO^5)$. Of these the first is that most usually obtained; the preparation of the others is more difficult, and depends on the temperature, quantity and nature of the lead salt.

$PbO, NO^5 + 3(3PbO + PO^5)$ is frequently formed when insoluble phosphates are dissolved in nitric acid and precipitated with acetate of lead, or when triphosphate of lead is boiled with dilute solution of nitrate of lead until no more is absorbed.

The phosphate of lead, crystallized before the blowpipe, has the composition of a triphosphate. On boiling the triphosphate of lead with a solution of chloride of lead, it increases so much in weight that the product must have the same formula as pyromorphite, $PbCl+3(3PbO+PO^5)$.

Tin Salt, a solution of protochloride of tin, furnished a precipitate with *c*-phosphate of soda which had the composition $3SnO+PO^5$.

Bismuth Salt.—Crystallized nitrate of bismuth gave, on digestion with *c*-phosphate of soda, a white precipitate, which, as no bismuth could be detected in the liquid and the precipitate contained no nitric acid, must have the formula $3BiO+PO^5+3HO$.

Cadmium Salt.—The precipitate which *c*-phosphate of soda produced in a solution of cadmium, was found in the air-dried state to consist of—

Oxide of cadmium .	63·41	$2\frac{1}{2}$ =	155·0	64·45
Phosphoric acid.....	loss	1	72·0	29·94
Water	5·74	$1\frac{1}{2}$	13·5	5·61

Archiv der Pharm., lix. p. 129.

On the Presence of Hippuric Acid in the Blood.
By F. Verdeil *and* C. Dollfus.

The blood which served for the experiments was collected by ourselves at the slaughter-house; and the experiments were repeated upon the blood of several oxen. Hippuric acid was found to be constantly present. We have succeeded in completely isolating this substance from the rest of the blood, but not in sufficient quantity for elementary analysis. We have however examined it with care, and are perfectly convinced that it is the same substance that is found in the urine of herbivorous animals, and which is called hippuric acid, from the form of the crystals seen under the microscope, and from their insolubility in cold water, their solubility in hot water, alcohol and æther; moreover, in fusing it is decomposed, and gives off the characteristic odour of benzoin.—*Comptes Rendus.* Dec. 24, 1849.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Red Pigments employed in painting upon Porcelain.
By M. Salvatat, *Chemist to the Manufacture Nationale de Sèvres.*

The red pigments for painting upon porcelain are of very great importance to the artist. It is by means of them that the figure painters obtain their carnations, and with their assistance and the colours derived from gold that the flower painters represent the red

and rose-coloured flowers. The landscape painters likewise frequently employ them.

These pigments are prepared with oxide of iron which has been submitted to a temperature varying with the tint required; for it is well known that the tint of oxide of iron varies from orange-red to a dark violet-red according to the temperature to which it has been exposed. The oxide of the tint required is mixed with 3 times its weight of the gray flux, composed of borax 1 part, sand 2, orange minium 6 parts, and ground without being fused.

Notwithstanding the simplicity of these proportions, and the easy preparation of the oxide of iron in a pure state, the red pigments for porcelain are classed with those colours which it is very difficult to obtain with all the desirable qualities.

The first beautiful reds were made by Dihl, who obtained them with an oxide which it is said he procured from Prussia. Bourgeois, an excellent chemist of Paris, likewise made some of great beauty; but the reds which have acquired the greatest celebrity are those prepared by M. Pannetier for Madame Jacquetot, and which shine in all their brilliancy in the master-works of that celebrated artist. The most skilful painters agree in admitting that these colours possess a liveliness of tint, a transparency and fusion, such as no other reds present.

The series of red pigments of M. Pannetier is composed of eleven tints, which descend from orange to gray in the following order:—

		Nomenclature used at Sèvres.
Orange	55	Orange-red.
Red No. 1	56	Capucin-red.
Red No. 2	58	Blood-red.
Red No. 3	62	Flesh-red.
Red No. 4	63	Carmine-red.
Red No. 5	64	Lake-red.
Violet from iron No. 6	66	Pale violet-red.
Violet from iron No. 7	66 A	Violet-red.
Violet from iron No. 8	66 B	Dark violet-red.
Violet from iron No. 9	66 C	Very dark violet-red.
Gray from iron	66 D	Gray from iron.

These tints, from the first to the last, form a series of types, which have sometimes been approached, but most frequently not, especially in the preparation of the extremes; in fact to this day nothing has been made to come near either the orange-red or the gray here in question.

I have thought it would be of some interest to ascertain whether oxide of iron alone was capable of giving this series of tints commencing with orange-red No. 55 and terminating with gray No. 66 D; and in case that these tints could be procured only with mixtures, to learn their nature and in what proportions they should be made. It also appeared useful to ascertain whether the flux employed by all chemists was perfectly identical with that used by M. Pannetier, the qualities of the latter being beyond all doubt.

And, lastly, I desired to learn whether the relative proportions of the flux and of the colouring principle were those given in the treatises on chemistry.

These several considerations led me to analyse the red pigments of M. Pannetier ; and the result of this investigation has enabled me to introduce several important improvements in the red pigments employed at Sèvres, based upon the analytical data which I now proceed to describe.

I. *Orange-red*, Pannetier; No. 55, *Orange-red*, Sèvres; *Orange, First Chromatic Circle*, Chevreul.

This colour corresponds in its tint with the orange of the first chromatic circle of M. Chevreul. I know of no chemist except M. Pannetier who has obtained from iron a tint approaching so closely to normal orange. All the experiments which I had made previous to these researches with pure oxide of iron constantly furnished a colour which was too red, agreeing with the capucin-red, which follows the pigment now under consideration. Analysis showed that M. Pannetier's orange contained oxide of zinc; this peculiarity perfectly explains the slight ochreous tone of the red in question. Compared with the orange of the first chromatic circle of M. Chevreul, the orange-red of M. Pannetier is slightly softened down (*rabattu*), that is to say mixed with traces of brown.

By treatment with hydrochloric acid, I found this pigment to contain silica, boracic acid, soda and oxide of lead, constituting the flux, and the oxides of iron and zinc with traces of alumina, forming the colouring principle. The quantitative analysis was made by the following process:—It was fused with carbonate of soda, which rendered the substance entirely soluble in nitric acid. The solution, evaporated to dryness, gave a deposit of silica, which was thrown upon a filter, washed, calcined and weighed. A current of sulphuretted hydrogen was then passed into the filtered solution, which threw down a large quantity of the sulphuret of lead mixed with sulphur, derived from the reduction of the persalt of iron by the hydrosulphuric acid. The sulphuret of lead, after being washed with water charged with sulphuretted hydrogen, was treated with fuming nitric acid, calcined, again moistened with sulphuric and fuming nitric acid, recalcined and weighed. The quantity of oxide of lead was deduced from the weight of the sulphate. The filtered liquid was neutralized with ammonia, then precipitated with hydrosulphate of ammonia, with which it was left in contact for twenty-four hours, so as not to carry down with it any boracic acid. The sulphurets of iron and of zinc thus obtained were collected on a filter, washed with water containing hydrosulphate of ammonia, and then heated with hydrochloric acid of the usual strength. It was filtered, boiled with nitric acid to peroxidize the iron, and thrown down with an excess of ammonia, which produced a copious precipitate of oxide of iron and alumina. These two oxides were separated by the usual processes; there was merely a trace of alumina present. The ammoniacal solution was precipitated with hydrosulphate of ammonia; the sulphuret of zinc, well washed, redissolved, and precipitated with

carbonate of potash; the precipitate, after being washed, was calcined and weighed. The solution, separated from the sulphurets of zinc and iron, contained neither lime nor magnesia. I had too little material at my disposal to determine directly the quantity of alkali and boracic acid; they were estimated by the difference, considering the loss as borax. It will be seen by the following analysis that this supposition was well founded:—

Silica	17·48
Oxide of lead	51·54
Borax	13·08
Oxide of iron	14·10
Oxide of zinc	3·80
Alumina	a trace

I have been able to produce without difficulty the orange pigment of M. Pannetier with a yellow tint, in which I had not succeeded by using pure oxide of iron, by forming an oxide composed of iron and zinc in the proportions above indicated. For this purpose 10 parts of metallic iron and 5 parts of distilled zinc are dissolved in cold muriatic acid, and the solutions mixed, precipitated with carbonate of soda, washed but not dried, until the exposure to the air and the oxygen of the water have caused the greenish deposit obtained on precipitation to pass into the state of peroxide. It is then dried and exposed to a dull red heat, and lastly mixed with 1 part of the oxide of the fourth orange-red for one of the above zinc oxide.

The latter compound oxide is mixed with a flux, consisting of sand, 1; fused borax, $\frac{3}{4}$; orange minium, 3; in the proportion of 475 parts flux for 100 of oxide. I shall subsequently have occasion to compare this flux with that for the gray, and will merely remark, that an excess of the flux tends to favour the development of the yellow tint peculiar to the silicate of lead and iron.

II. *Red No.* 1, Pannetier; *No.* 56, *Capucin-red*, Sèvres; *Fourth Orange-red*, *First Chromatic Circle*, Chevreul.

This red, which appears less yellow to the eye than the preceding, and consequently approaches more closely to pure red, is easily obtained with pure oxide of iron. It is the most orange-red which it has hitherto been possible to obtain with pure anhydrous oxide of iron: I say anhydrous and pure; for the hydrated oxide of iron, in which the water may be replaced by oxide of zinc, and probably also by other oxides, without the tint being modified even at a bright red heat, is of a yellower shade, but *rabattu*, and is known by the name of ochre or yellow-brown.

Analysis indicated the same elements in this pigment as in the one which precedes, with the exception of the oxide of zinc, which is entirely wanting. A trace of alumina was likewise found.

The quantitative analysis was made with a view to estimate directly the soda which was supposed to exist in the state of borax. The silicic acid was consequently estimated from the loss.

The pulverized substance was decomposed with hydrofluoric acid; the fluorides, evaporated to dryness, were converted into sulphates,

and these into sulphurets, by the addition of sulphuretted hydrogen to the slightly acidified mixture. The oxide of lead was estimated in the state of sulphate as above, the excess of sulphuretted hydrogen expelled, the iron peroxidized by a current of chlorine, and then thrown down with ammonia. The oxide of iron was separated from alumina as above. The liquid, freed from lead, alumina and iron, was evaporated to dryness, the residue melted in an atmosphere of carbonate of ammonia, and weighed. From the weight of sulphate the quantity of soda was calculated, which gave the corresponding amount of borax. No lime nor magnesia could be detected. Analysis gave—

Silica	16·60
Oxide of lead	50·39
Borax	12·51
Oxide of iron	20·50
Alumina	a trace

The oxide of iron of the above tint is prepared by calcining, at the lowest possible temperature, the sulphate of the protoxide of iron. It ought however to retain the tint in question at a temperature corresponding to 800° C. There is no inconvenience in not attaining this degree of temperature; it is even preferable to remain below it. The oxide is washed with hot water and dried.

III. *Red No.* 2, Pannetier; *No.* 58, *Blood-red*, Sèvres; *Third Orange-red*, *First Chromatic Circle*, Chevreul.—This red, which contains still less yellow than the capucin-red, is obtained with pure oxide of iron, prepared by decomposing the sulphate of the protoxide by heat, and submitting it to a somewhat higher temperature than in preparing the oxide for the fourth orange-red. The analysis was made as above described; the borax in this and the following analyses was obtained by the difference; it is therefore always increased by the loss occasioned in the manipulation. This pigment was found to be composed of—

Silica	16·90
Oxide of lead	49·51
Borax	13·39
Oxide of iron	19·70
Alumina	0·50

IV. *Red No.* 3, Pannetier; *No.* 62, *Flesh-red*, Sèvres; *Second Orange-red*, *First Chromatic Circle*, Chevreul.—The name of this pigment indicates pretty fairly its tint; it is more red than the preceding. It will not be without interest to state in this place, that it is the purest red which has been attained upon porcelain; and we must mention it to our shame, but to the praise of the artist, who, by careful combinations and happy contrasts, has been able not merely to do without it, but even to make believe that he possessed this pigment. We must confess that the pallet of the porcelain painter is deficient in reds, and that all the pure tints corresponding to the first orange-red, to orange-red, to the fifth, fourth, third, second, first red, to red, to the fifth, fourth, and third violet-

red, have never hitherto been made in vitrifiable pigments. This is a deficiency which it is difficult to fill up at the present day, but it is the only one. The circle comprises seventy-two colours, and I have succeeded in making the other sixty by very simple means, which I intend shortly to publish, in order to extend the use of the chromatic table, which must render very important services to the arts and sciences.

In red No. 3 of M. Pannetier there was found—

Silica	16·60
Oxide of lead	49·18
Borax	14·22
Oxide of iron	20·00
Alumina	trace

V. *Red No.* 4, Pannetier; *No.* 63, *Carmine-red*, Sèvres.

VI. *Red No.* 5, Pannetier; *No.* 64, *Lake-red*, Sèvres.

VII. *Iron-violet*, Pannetier; *No.* 66, *Pale Violet-red*, Sèvres.

VIII. *Iron-violet No.* 7, Pannetier; *No.* 66 *A, Violet-red*, Sèvres.

The designation used at Sèvres for these reds gives a pretty accurate idea of the differences of tints which distinguish these colours. They belong to the circles which comprise the *rabattu* colours, and no longer occur in the first chromatic circle of M. Chevreul. I shall merely make known their composition:—

	V.	VI.	VII.	VIII.
Silica	16·30	16·40	16·85	16·39
Oxide of lead	50·02	49·44	50·66	50·52
Borax	13·68	15·96	12·66	12·01
Oxide of iron	20·00	18·20	19·83	21·08
Alumina	trace	trace	trace	trace

All these oxides are procured by submitting the peroxide obtained by the decomposition of the protosulphate of iron by heat to higher and higher temperatures.

IX. *Iron-violet No.* 8, Pannetier; *No.* 66 *B, Dark Violet-red.* Sèvres.

Pure oxide of iron, calcined at a very bright heat, is not capable of furnishing a darker shade than the violet No. 7. All the experiments which I have made to obtain a darker violet led to no result. I therefore examined whether the oxide of iron contained in the violet No. 8 was free from other oxides, and readily detected the presence of manganese:—

Silica	16·56
Oxide of lead	50·09
Borax	15·36
Oxides of iron and manganese	17·99
Alumina	trace

X. *Violet from Iron No.* 9, Pannetier; *No.* 66 *C, Very dark Violet-red*, Sèvres.

The shade of this colour is so dark, that to the eye it merely retains a slight tint of blue. It also contains oxide of manganese in-

timately combined with the oxide of iron. It is present in greater quantity than in the preceding violet, and to it is owing the distinctive force of this colour. The oxides of iron and manganese were in this case separated by succinate of ammonia:—

Silica	16·40
Oxide of lead	50·60
Borax	12·14
Oxide of iron	18·71
Oxide of manganese	2·15
Alumina	trace

XI. *Gray from Iron No.* 10, Pannetier; *No.* 66 *D, Iron-gray,* Sèvres.

This colour is much sought after; and as its tint is pretty black and sufficiently intense, it is most frequently used by figure-painters, who employ it advantageously to separate the flesh-tints, without fear of seeing them blacken beyond what is desired by the fire. It does not contain any oxide of cobalt, but a pretty considerable amount of oxide of manganese:—

Silica	17·09
Oxide of lead	47·30
Borax	17·01
Oxide of iron + Oxide of manganese	18·60
Alumina	trace

The oxides used for making the pigments Nos. 66 B, 66 C and 66 D are prepared according to the same method as that described for the preceding reds. The introduction of the manganese into the mixture is a very delicate operation. I shall return to this subject in a special paper, treating of the influence of molecular changes on the properties of several metallic oxides.

From the preceding analyses it is seen that the iron pigments of M. Pannetier are all composed, with trifling exceptions, of the same elements combined in the same proportions, especially if in each pigment the alumina, the oxides of iron, zinc and manganese are united. It is at once perceived that the flux is the same; the colouring matter alone varies; and we have pointed out that this variation depends either on the intensity of the heat to which the oxide has been submitted, or on the nature of the elements which enter into its composition, or lastly, on the proportions in which these elements are combined.

The mean of all the analyses above given leads to the following numbers:—

	Relations.		Relations.	
Silica	1	16·72		
Oxide of lead	3	49·93	80·47	4 flux
Borax	¾	13·82		
Oxides Fe^2O^3, Mn^2O^3, Al^2O^3, ZnO		19·53	19·53	1 oxide

Theory, starting from the relations above indicated, would give—

	Relations.			Relations.
Silica	1	16·85		
Oxide of lead	3	50·55	80	4 flux
Borax	¾	12·60		
Oxides Fe^2O^3, Mn^2O^3, Al^2O^3, ZnO		20·00	20	1 oxide

The numbers agree as closely as possible; the borax alone is in slight excess, but this bears any loss that may have been incurred. In two determinations of the borax by direct experiments, 12·51 and 12·12 were found, which approach more closely to the calculated number.

We are now able to compare the composition of these red pigments with those of other chemists. They are composed of—

	Relations.			Relations.
Silica	1	16·67		
Oxide of lead	3	50·00	75	3
Borax	½	8·33		
Oxide of iron		25·00	25	1

Comparing these figures with those which precede, we are compelled to admit that the quantities of lead and sand being constant, a quantity of oxide in the former is replaced by its weight of borax. This will instantly explain the influence of such substitution on the fusibility of the pigment. The difference which exists between the two series of pigments may be rendered still more clear. In M. Pannetier's colours the flux is composed of sand, 1 part; borax, ¾; and minium, 3; a compound which is more fusible than that which contains only ½ part borax. In the same pigments we find, for 1 part of colouring oxide, 4 parts of flux, whilst in the other colours we find 1 part of colouring oxide only for 3 parts of flux, a modification which increases the fusibility of the colour.

I shall not dwell longer on the cause of the superiority of the pigments under consideration. With respect to the glaze, this superiority is quite evident from what precedes. I now come to the question of the brilliancy and vivacity of the tint, and I think it will be solved in as simple a manner by what follows.

I have already stated that the difference of tint which oxide of iron acquires (and in this case we speak only of pure oxide) depends on the temperature to which it has been exposed. I will now add that all these tints are not permanent; the higher the temperature, the more vigorous the tone. I will also call to mind that the colours which the oxide assumes vary from orange to violet, that is to say, that they may be decomposed into yellow, red and blue—simple colours, which give a more or less dark gray according to the degree of intensity of the three elementary colours. The lower the temperature, the more yellow does the pigment contain; the higher the temperature, the more there is of blue.

From this it appears evident to me that the colour would be the purer according as the oxide producing it is formed of identical molecules, in regard to the modifications they have experienced by

the same temperature. The tint will therefore be perfectly pure if all the molecules have been exposed to the temperature requisite to develope it; if none have been exposed to too high a temperature, capable of modifying it; either to too low a temperature, which would leave too much yellow; or to too high a temperature, which would increase the amount of blue. The manipulation must therefore consist in composing the colour only of particles of oxide which have been exposed to the same temperature. This is easily attained by operating only upon small quantities at a time, and agitating the mass constantly. When the temperature has been maintained for a sufficient time, the fire is removed, all the successive preparations are dried, and only those which present the same shade mixed with each other.

I have carefully examined the part which alumina acts, some chemists regarding it as advantageous, and even indispensable, for the easy preparation of transparent reds. I have assured myself, in the course of this investigation, that it is of no importance. The reds of M. Pannetier, with the exception however of the orange, in a sample of which I found a considerable quantity replacing oxide of zinc, contained but mere traces of alumina; and specimens which I prepared, containing a certain proportion of that oxide, exhibited no superiority over the reds made with oxides containing none.

To place this beyond all doubt, I purchased of M. Colcomb Bourgeois four samples of oxides called *mars*. They contained—

	No. 1. Orange.	No. 2. Red.	No. 3. Lake.	No. 4. Violet.
Sand	6·80	7·04	2·80	9·00
Oxide of iron	88·00	85·66	82·70	76·00
Alumina	5·00	7·04	14·00	14·40
Lime	..	..	..	0·50
Loss	0·20	0·26	0·50	0·10

I mixed them with 4 parts of M. Pannetier's flux, and baked the colours thus prepared on some Sèvres porcelain. The result did not differ from that obtained with oxides containing no alumina; and nevertheless the amount was considerable, especially in Nos. 3 and 4.

I do not pretend to exclude all the properties of alumina; perhaps in the case of *mars* for miniature painting or for oil painting, it has the advantage of diluting or of enlivening the colour, but I believe that it is of no use in the preparation of vitrifiable pigments. —*Ann. de Chim. et de Phys.*, Nov. 1849.

Disinfecting Compound.

M. Herpin recommends dried and pulverized plaster of Paris, mixed with rather more than one-fifth of its weight of powdered charcoal, as a cheap and most effective disinfecting mixture. It entirely removes the noxious emanations from decomposing organic matters, fixing the ammonia, and forming finally a valuable manure. —*Journ. de Pharm.*, Dec. 1849.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Nitrates of Iron and some other Nitrates.

By JOHN M. ORDWAY*, *Massachusetts.*

SESQUINITRATE of iron may be easily obtained in the form of crystals by taking advantage of the fact, that this salt is almost insoluble in cold nitric acid.

When metallic iron is gradually added to nitric acid of spec. grav. 1·29, copious red fumes are given off, and the liquid assumes a greenish hue, till nearly 10 per cent. of iron has been taken up. A further addition changes the colour to a dark red; and if the action be continued still longer, a rusty precipitate forms. If we stop short of this last point, and add to the product its own bulk of nitric acid of spec. grav. 1·43, an abundant crop of crystals will be deposited on cooling below 60° F. The same result may be attained by evaporating the greenish liquid, and adding acid enough to insure a considerable excess, before setting the solution aside to cool. If the first crystals are brown, they may be purified by redissolving in nitric acid, with the aid of a gentle heat, and allowing again to crystallize.

The crystals thus obtained have the form of oblique rhombic prisms, which are either colourless or of a delicate lavender colour,

* The author observes as follows in a letter relating to his investigations:—

Those who have occasion to prepare liquid nitrate of iron in the large way are often troubled in cold weather by the deposition of crystals before the requisite quantity of iron has been dissolved. Concerning the true nature of these crystals, I have been unable to gather any definite information from any of the works of chemistry within my reach. Indeed, respecting the compounds of nitric acid and peroxide of iron, though of some importance in the arts, the books give but vague accounts, and those not altogether correct. Thus "azotate ferrique" is described in Hoeffer's 'Dictionnaire de Chimie et de Physique' as "d'un brun rouge, *incrystallisable*, deliquescent, soluble dans l'eau et dans l'alcool." While Berzelius incidentally mentions that "*Vauquelin* ayant laissé l'acide nitrique en contact avec de la battiture de fer, trouva, au bout de plusieurs mois, des *cristaux incolores*, qui affectaient la forme de prismes rectangulaires à quatre pans." Perhaps the *rectangulaire* was a mistake, for in several experiments I have obtained forms variously modified, but all referable to the oblique rhombic system. In one huge crystal, which had been many months in forming, the angles included between the long lateral faces of the prism were found to be 101° and 79° nearly.

Numerous experiments, made with a view to obtain more light on the subject, have afforded some results which may not be altogether uninteresting, and are, I trust, partly new and singular.

but when dissolved in water yield a yellowish-brown solution. They are somewhat deliquescent, and very soluble in water; while at a temperature below 60° F. a weighed quantity was not wholly taken up by more than 20 parts of nitric acid of spec. grav. 1·37.

At about 117° F. this salt melts into a clear deep red liquid, which in one trial remained fluid till cooled to 83° F., when the heat developed by solidification quickly raised the thermometer to 116½°.

The composition of this substance, as indicated below, affords reasons for supposing that by its admixture with a bicarbonate an intense cold might be produced. Such proved to be the case, for when 2 oz. of the bruised crystals were stirred up with 1 oz. of pulverulent bicarbonate of ammonia, the thermometer introduced fell from 58° to −5° F. Previous cooling is attended with an increase of effect.

These experiments being very tangible, would furnish excellent illustrations of the principles of latent heat.

A small quantity of the melted nitrate, kept hot for several hours by means of a water-bath, yielded a perfectly dry, dark brown deliquescent powder, containing some water and one-half the original amount of acid. More acid may be expelled by a moderate heat, but to drive off the last portions requires a temperature approaching redness.

The well-drained crystals afforded by precipitation with ammonia 19·8 per cent. of peroxide of iron; and 100 grs. boiled with carbonate of baryta gave a liquor which with sulphuric acid yielded 86·5 grs. of sulphate of baryta, indicating 40·104 per cent. of dry nitric acid. Hence the formula is probably $3NO^5, Fe^2O^3 + 18HO$, which would give in 100 parts,—nitric acid, 40·095; peroxide of iron, 19·819; water, 40·086.

Basic Nitrates.—A liquid is used in cotton-dyeing, which is prepared by adding iron turnings to aquafortis till the solution assumes a very dark red colour. A fair sample of this solution, of spec. grav. 1·478, was found by analysis to contain 5 equivs. of nitric acid to 2 equivs. of sesquioxide of iron. A portion of the same, placed in contact with metallic iron, remained clear until nearly enough iron had been taken up to form a sesquibasic nitrate ($2NO^5, Fe^2O^3$), when a rusty precipitate began to appear, whose exact nature it is difficult to determine.

A full sesquibasic nitrate was formed by adding crystals of the nitrate to the proper quantity of freshly-precipitated oxide of iron. And proceeding by the same means, but with slow and cautious steps, as into an unknown region, I was successively astonished by the discovery of soluble basic nitrates containing, to 3 equivs. of acid, 2, 3, 6, 8, 12, 15, 18 and 24 equivs. of base respectively; and then, from the slowness with which the union took place in the last, I supposed the limit reached. Yet this liquid was found to bear the addition of a small quantity of lime-water without change.

On arriving at these remarkable results, the question naturally arose, whether there were any chances of error. But on examination no foreign substance was detected; and the analyses of the

6, 12, 15 and 24 basic compounds agreed so nearly with the syntheses as to remove all doubts.

Which of these bodies have claims to be regarded as true atomic compounds, there seems to be no clue but analogy to determine. They all form intensely deep red liquids, which are not altered by dilution nor by brisk boiling provided the evaporation be not carried too far. By spontaneous evaporation they leave a very dark red powder, perfectly soluble in water. That left by the dodecabasic nitrate was not deliquescent, and lost 30 per cent. of its weight by ignition. Hence its empirical composition would be NO^5, $4(Fe^2O^3)+9HO$.

When cotton cloth is dipped in any of these solutions, and dried, the oxide of iron becomes permanently attached. Indeed the adhesion of the base to cotton fibre renders filtration through paper exceedingly slow.

Since spring and river water, and the solutions of most salts, are incompatible with the 24 basic nitrate, it was found necessary to use an abundance of distilled water for washing the oxide used in its preparation. So intense was the colour of this liquid, that, though containing only 3·4 per cent. of oxide of iron, 2 drops imparted a perceptible tinge to a pint of distilled water. In trying the reactions of various substances with it, all the iron appeared to be immediately thrown down by muriate of ammonia, chloride of sodium, iodide of potassium, chlorate of potash, sulphates of soda, lime, zinc and copper, nitrates of potash and soda, and the acetates of baryta and zinc. Precipitates formed more slowly with the nitrates of ammonia, magnesia, baryta and lead. Tartrate of soda furnished a precipitate soluble in ammonia. Ferrocyanide of potassium gave a dark peat-brown precipitate without the least tinge of blue. Ferrocyanide of potassium gave likewise a rich peat-brown precipitate. Tincture of galls afforded dark brown flakes, and on standing some time the supernatant liquor turned black. Alcohol, acetate of lead, acetate of copper, cyanide of mercury, nitrate of silver and arsenious acid caused no change.

With the tribasic nitrate, muriate of ammonia, chloride of sodium and nitrate of soda produced no effect; while the sulphates threw down all the iron, prussiate of potash struck a blue colour and tincture of galls gave a black.

Nitrate of Alumina.—Nitrate of alumina crystallizes from a concentrated and somewhat acid solution, in colourless, oblique, rhombic prisms, whose length is generally small in proportion to their width. They are deliquescent, and very soluble both in water and in nitric acid. The crystals, like those of the other sesquinitrates, can be best dried by spreading them on an absorbent surface, and placing the whole under a bell-glass with a shallow vessel containing sulphuric acid.

The salt was found to melt at 163° F. into a clear colourless liquid, which began to crystallize when cooled down to $147\frac{1}{2}°$, the thermometer rapidly rising at the same time to 162°. The melted mass parts with its acid much less rapidly than the nitrate of iron.

1 oz. of the powdered salt mixed with ½ an oz. of bicarbonate of ammonia lowered the thermometer from 51° to −10° F.

100 grs. of pretty dry crystals yielded by ignition 13·7 grs. of alumina. Distillation with sulphuric acid gave 42 per cent. of nitric acid; and by boiling with carbonate of baryta, 42·42 per cent. was separated. The numbers corresponding to $3NO^5, Al^2O^3 + 18HO$ would be in 100 parts,—nitric acid, 43·17; alumina, 13·68; water, 43·25.

Nitrate of alumina appears to form with the hydrate a series of salts similar to the basic nitrates of iron. But they have not as yet been fully examined.

Nitrate of Chrome.—Nitrate of chrome crystallizes with difficulty in warm weather; but I have succeeded in obtaining two crops, one of them presenting the form of the oblique rhombic prism, and the other an extremely modified variety of the same. These crystals have the changeable purple colour peculiar to the salts of chrome, and their solution in water is of the same hue while cold, but becomes green when heated.

This salt fused at about 98° F. into a deep green fluid, which began to assume the solid state when cooled to 75°, the thermometer rising thereupon to 96°. If heated to redness, it undergoes complete decomposition, leaving a bulky oxide of a beautiful green colour.

The composition of nitrate of chrome was found by analysis to be,—nitric acid, 39·7 per cent.; oxide of chrome, 19 per cent. Calculation from the formula $3NO^5, Cr^2O^3 + 18HO$ gives,—nitric acid, 40·44; sesquioxide of chrome, 19·13; water, 40·43.

No experiments have been made on the basic salts.—Silliman's *Journal*, January 1850.

On the Formation of Succinic Acid from Butyric Acid.
By M. Dessaignes.

M. Gerhardt, in his 'Précis de Chimie Organique,' observes, that parallel with the series of monobasic fatty acids whose general formula is $C^mH^mO^4$, a series of bibasic acids may be constructed whose general formula is expressed by $C^mH^{m-2}O^8$. Almost all the acids of these two parallel series are simultaneously produced when fatty bodies possessing high equivalents are oxidized by nitric acid; and it is conceivable that each term of the bibasic series is formed by a simple oxidation of the term corresponding to it in the monobasic series. If, however, we except the acetic and oxalic acids, the possibility of this transformation remains to be demonstrated experimentally.

Succinic acid corresponds to butyric acid in the series of the fatty acids. I have succeeded, in fact, in producing it by the oxidation of the latter acid. In an apparatus composed of a retort, a long tube and a receiver, ground and fitted into each other without cork, I heated about 30 grms. of very pure butyric acid, which had been prepared by the fermentation of flesh and starch, with twice its

volume of nitric acid of spec. grav. 1·40. The apparatus was inclined so that the condensed vapours of the butyric acid fell back into the retort, and nitric acid was added from time to time. Although a red atmosphere of nitrous gas was continually visible above the mixture, the action was very slow, and it was far from being complete at the end of ten days of twenty-four hours each. Seeing no end to the appearance of red vapours, I distilled the liquid with precaution until I obtained a crystalline residue. This residue was contaminated with a substance which attracted moisture from the air, and from which I was unable to free it by the continued heat of the water-bath. I pressed it strongly between folds of paper, and in this manner obtained it sufficiently pure to submit it to some experiments. I easily observed that the crystals exhibited all the physical characters and reactions of succinic acid. I had not sufficient matter to purify it completely, and to submit it to direct analysis; but I prepared and calcined the silver salt, on which most reliance could be placed; 0·471 grm. left 0·303 of silver, which gives 64·33 per cent. of silver; theory requires 65·05.—*Comptes Rendus*, Jan. 21, 1850.

On some Compounds of Nitroharmalidine. By J. Fritzsche.

Nitroharmalidine and Oxide of Silver.—A combination of nitroharmalidine with oxide of silver is obtained when a perfectly neutral salt of nitroharmalidine is mixed with a solution of oxide of silver in ammonia. Such a solution, free from all excess of ammonia, is obtained by adding ammonia to a solution of nitrate of silver until the resulting precipitate is redissolved. To this solution a small quantity of a neutral solution of nitrate of nitroharmalidine was added, and the liquid filtered from the precipitate employed for preparing the compound. This liquid, on being mixed with a neutral solution of the nitrate of nitroharmalidine, gave a copious bulky gelatinous precipitate of a yellowish-red colour, which it was found best to leave for some time in the liquid, when it contracts somewhat, and can then be more readily filtered and washed than immediately after precipitation. A gelatinous mass is obtained on the filter, of the appearance of a recently precipitated mixture of alumina and peroxide of iron, which also shrinks similarly on drying and acquires a dark brownish-red colour.

This compound is insoluble in water and but sparingly soluble in alcohol; it is instantly decomposed by acids, and is also decomposed by ammonia in the cold, oxide of silver being dissolved, and in the place of the compound which has disappeared an alkaloid separates in distinct crystals. Analysis gave—

	Found.		
Nitroharmalidine.....	68·44	3315·66	= 69·579
Oxide of silver	30·00	1449·69	30·421

Nitroharmalidine and Nitrate of Silver.—There appear to exist at least two compounds of nitroharmalidine with nitrate of silver.

When, for instance, an alcoholic solution of the alkaloid is mixed with a solution of the silver salt, there separates, according to the concentration and temperature of the solutions, either immediately or only after cooling and standing, a compound in bulky flakes, consisting of a matted tissue of needles; at the same time with this compound there generally separates another one in dark orange-yellow crystalline granules. These compounds have not yet been further examined.

Nitroharmalidine and Petroleum.—When a solution of nitroharmalidine in petroleum is allowed to cool, two distinct crystalline products generally separate, one of which consists of roundish granules of the orange-yellow colour of nitroharmalidine, the other of needles of the light yellow colour of the salts of this alkaloid. The orange-yellow granules appear to be unaltered alkaloid, whilst the light yellow needles are a combination of it with petroleum. Sometimes this combination may be obtained in a pure state, that is, free from any admixture of the granules; this result however was only obtained once. As the separation of the granules commences earlier than that of the needles, it is most easily prepared by quickly filtering the solution at the right moment during the cooling. Moreover, the needles dissolve far more readily than the granules, when the liquid, after complete precipitation, is again heated with the precipitate. When therefore it is filtered after the greater portion of the needles has redissolved, we obtain on cooling a far purer preparation. The combination of nitroharmalidine with petroleum forms minute matted needles, but still distinctly perceptible to the naked eye, of the light yellow colour peculiar to the salts of this alkaloid; it has a faint odour of naphtha, but is not altered by exposure to the air, either at the ordinary temperature or on drying in the water-bath. Water has no influence upon it at the ordinary temperature, but on ebullition it decomposes it. When alcohol is mixed with the compound, it instantly decomposes it, and the light yellow colour changes into the orange-yellow of the alkaloid. Acids likewise produce decomposition, when the separation of the petroleum may be distinctly observed under the microscope. According to an approximative analysis, this compound appears to contain 6 per cent. of petroleum.

Hydrocyannitroharmalidine.—Nitroharmalidine furnishes with hydrocyanic acid a compound which cannot be regarded merely as a salt of hydrocyanic acid. It is, like hydrocyanharmaline, a body of peculiar constitution. The formation of this substance may be traced under the microscope, when a small quantity of crystallized nitroharmalidine is placed between two glass plates, and then a drop of alcoholic solution of prussic acid added. It is then seen that at first the crystals dissolve superficially, but almost instantaneously where the alkaloid has disappeared the new compound separates in microscopic spherical masses, which sometimes exhibit a crystalline structure, into which, according to the concentration of the acid and size of the crystals, the alkaloid is completely changed more or less quickly, not unfrequently indicating the former

position, and even the form of the crystals. Hydrocyannitroharmalidine is obtained on a large scale precisely in the same manner as directed for hydrocyanharmaline. Either nitroharmalidine is dissolved with the assistance of heat in an alcoholic solution of prussic acid, and allowed to cool slowly, when the compound separates in very minute acicular crystals; or a concentrated solution of acetate of nitroharmalidine is mixed with concentrated hydrocyanic acid and set aside for some time, when very slender acicular crystals of the new compound gradually separate; or lastly, a cold aqueous solution of a salt of nitroharmalidine, mixed with an excess of hydrocyanic acid, is precipitated by ammonia. In this last method the liquid becomes turbid towards the end, but soon the hydrocyannitroharmalidine separates as a transparent, and with concentrated solutions, solid jelly. In the course of some time this jelly becomes turbid, and is converted into very minute microscopic crystals. The gelatinous substance is very probably a hydrate of the new compound, which under certain conditions, a low temperature for instance, presents greater stability, and, partially retaining its gelatinous condition, contracts into roundish masses.

Prepared according to one of the two first methods, hydrocyannitroharmalidine forms acicular crystals of the pale yellow colour peculiar to the salts of nitroharmalidine. In the moist state it readily parts with hydrocyanic acid by exposure to the air; but, once dried, it is permanent, and may even be exposed to a gentle heat without decomposition. When boiled with water, it parts, like hydrocyanharmaline, with hydrocyanic acid, the nitroharmalidine dissolves in the water, and separates in crystals on cooling. It is not decomposed by dilute ammonia, as is evident from its mode of formation; but when acted upon by strong ammonia, decomposition takes place, which is recognized by the colour becoming darker, and also from the change of form seen under the microscope. This decomposition is effected more rapidly by caustic potash; consequently the combination is much more feeble than in the case of hydrocyanharmaline. Nevertheless hydrocyannitroharmalidine must not be looked upon as a salt, but as a compound of a peculiar kind, and its behaviour towards sulphuric acid favours this view. It dissolves in this acid at the ordinary temperature, without any evolution of hydrocyanic acid, to a brownish-yellow liquid, which even after careful dilution by dropping it into cold water gives off no odour of hydrocyanic acid. When too much water has not been used, the pale yellow solution soon grows turbid, and then deposits minute acicular crystals of a compound which contains nitroharmalidine, hydrocyanic acid and sulphuric acid. It was impossible to ascertain the relative proportions of the constituents; for as soon as it was attempted to separate the crystals from the acid mother-liquor by washing on a filter, decomposition immediately ensued, as distinctly evidenced by the odour of hydrocyanic acid. These phænomena however appear to indicate that the crystals precipitated by water from the sulphuric solution form a sulphate of hydrocyannitroharmalidine; and it is extremely probable that, like hydrocyanharmaline, it is a base, the

salts of which, however, are still more readily decomposed than those of hydrocyanharmaline into hydrocyanic acid and the corresponding salts of the primary alkaloid. As some theoretical speculations respecting the rational formula of nitroharmalidine are connected with the ascertaining of this point, inasmuch as it is impossible to conceive how nitroharmalidine, which must be regarded according to Berzelius' view as $(C^{27}\,H^{10}\,N^{2}\,O^{2})\,O + NO^{3} + NH^{3}$, can take up hydrocyanic acid into its conjunct, the author has endeavoured to prepare other salts of hydrocyannitroharmalidine. He obtained under the microscope crystalline products; but as not only none of them differ from the corresponding salts of the primitive alkaloid in so characteristic a manner as is the case with the muriate of hydrocyanharmaline, but on the contrary all have exactly the appearance of the corresponding salts of nitroharmalidine, and negative results were obtained in experiments upon a large scale, the question cannot be now decided. In the analysis of hydrocyannitroharmalidine, the author obtained—

Nitroharmalidine		3315·66	= 90·754
Hydrocyanic acid	8·85	338·78	9·246

When nitroharmalidine is heated in a bath of chloride of calcium, it melts when the temperature of the bath has risen to about 248°, and sometimes even when slightly above 212°, to a resinous dark brownish mass, which on cooling again solidifies. No volatile products appear to escape, as such an inconsiderable loss in weight was observed that it could be explained from the escape of the last traces of moisture adhering to the pulverulent alkaloid; but in this operation, whilst a large portion of the alkaloid remained unaltered, the rest became converted into a substance possessing considerable resemblance to the metamorphic product above described. The latter can be separated from the unaltered alkaloid either by exhausting the finely-pulverized fused mass repeatedly with boiling water as long as this removes any nitroharmalidine, or by first dissolving the fused mass in acetic acid, with which it forms a clear solution, and adding nitric acid to this after sufficient dilution with water. This precipitates the metamorphic product, whilst the nitrate of nitroharmalidine remains dissolved, and can be obtained by evaporating the filtered solution. But this and some other products of decomposition have not yet been examined by the author.—*Bulletin de St. Pétersbourg*, viii. p. 81.

On the Melting-point of Stearine from Mutton Suet.
By Dr. W. Heintz.

When stearine prepared from mutton suet, after being purified by six to eight crystallizations from the ætherial solution, is enclosed in a capillary tube and heated in a water-bath, it melts apparently at 124°–126° F., becoming perfectly transparent. As the temperature rises, it becomes opalescent, and at about 136° F. reacquires almost its former opacity. Finally, when the temperature has risen

to 144°, the stearine melts perfectly. On the other hand, when a thin layer of the stearine, which has resolidified after melting, is immersed in water at a temperature of 126°, it completely retains its form, notwithstanding that it becomes perfectly transparent. Hence it follows that the stearine from mutton suet becomes transparent at 124°–126°, but by no means liquid. The explanation of this remarkable phænomenon the author reserves for a future notice.—*Ber. d. Berl. Akad.*

On Dulcose, a Homologue of Grape-Sugar. *By* A. Laurent.

In 1843 M. Gerhardt conceived the idea of comparing the properties of organic substances with their composition, setting aside all hypotheses as to the arrangement of the atoms, and he arrived at the following conclusion:—*If two bodies have such a composition that that of the one can be represented by that of the other* $+n$*-times* CH^2, *these two bodies will possess analogous properties* (*except in cases of isomerism*). Thus the formic, acetic and metacetic acids have analogous properties, because they contain O^2+CH^2, O^2+2CH^2, O^2+3CH^2. It is the same with the hydrurets of benzoyle and cumyle, the benzoic and cuminic acids, whose composition is represented by—

Hydrurets ..... C^7H^6O, $C^7H^6O+3CH^2$.
Acids ..... $C^7H^6O^2$, $C^7H^6O^2+3CH^2$.

M. Gerhardt calls all those bodies homologues which only differ from one another by nCH^2.

As the most striking examples which he first brought forward were derived from the series of compounds formed by the alcohols of methyle, ethyle, amyle, and as the analogy of these substances was already sufficiently explained either by the theory of radicals or by the numerical relations which I had pointed out in that series, chemists paid no attention to homology, looking upon it as a classification in the form of a dictionary.

However, for the last year or two fresh examples of homology have been discovered among some bodies possessed of rather singular properties, and in all cases the analogy of the properties has been apparent. I will merely mention a few of the most remarkable. Sarcosine, leucine and glycocolle are three bodies which are extracted from flesh, and which possess considerable analogy; the composition which was assigned to them did not make them homologous. In conjunction with M. Gerhardt I have repeated the analyses of the two latter, and we have found that all three conform to the law of homology *.

The bile of the pig contains an acid, which is homologous with the acid contained in ox-bile.

* M. Mulder, to whom we owe the first analyses of leucine, disputes our formula; but our analyses have been confirmed by those of Cahours and Strecker. M. Mulder has already confessed to the error which he had committed on glycocolle. We do not despair therefore of seeing him adopt our formula for leucine.

The salicylic and anisic acids give rise to two grand series of compounds. The starting-points having been corrected by my analyses, and M. Gerhardt having signalized them as homologues, the homology has held good in all the derived substances, as M. Cahours has recently shown. The organic alkali contained in tea and that which occurs in cacao have been found homologous.

Mannite is found to have considerable analogy with erythromannite, obtained by Dr. Stenhouse from certain colouring lichens. But this chemist assigns to the latter substance a formula which has no relation of homology with mannite. M. Gerhardt, supposing a slight error in the analysis of this substance, considers that it should be viewed as a homologue of mannite. But, on this hypothesis, nitric acid would furnish with erythromannite a sexnitrated substance, the sole example known in organic chemistry. Recently however M. Strecker has proved, by fresh analyses, that nitromannite itself is sexnitrated, and not quintinitrated, as had been supposed.

I have now a very remarkable example to add to the list of homologues; it is a new species of sugar, which comes from Madagascar, the origin of which however is not well known. It crystallizes in oblique rhombic prisms, possesses a slight sweetish taste, and diffuses upon incandescent charcoal the same odour as sugar. From its composition it is homologous with grape-sugar. Deprived of water by fusion, it contains $C^{14}H^{28}O^{12}$; deducting C^2H^4, we have $C^{12}H^{24}O^{12}$, or grape-sugar. When redissolved in water, it combines with 3 atoms.

Like grape-sugar, it acts the part of a weak polybasic acid, for it can exchange 4 atoms of hydrogen for 4 atoms of barium, furnishing a well-crystallized salt, which contains $C^{14}H^{24}Ba^4O^{12}+14Aq$.

The action which nitric acid exerts upon it is interesting. It is well known that the homologous bodies of the grand series nCH^2 yield with oxidizing agents the homologous acids of that series. It is equally known that grape-sugar furnishes with nitric acid saccharic acid, whilst the gums and milk-sugar, which are so closely related to grape-sugar, give mucic acid, which is isomeric with saccharic acid. Now the new substance is likewise converted into mucic acid by the action of nitric acid.

According to M. Biot, it exerts no action upon polarized light; and according to M. Soubeiran, it does not undergo alcoholic fermentation.—*Comptes Rendus*, Jan. 1, 1850.

Notice on the Composition of Leucine. *By* A. Strecker.

This substance was first analysed by Mulder, who expressed its composition by the formula $C^{12}H^{12}NO^4$. Recently Laurent and Gerhardt, and also Cahours, have advanced the formula $C^{12}H^{13}NO^4$ for this substance, and have found for its combinations with acids a composition corresponding to the above formula. Since however Mulder has recently controverted these statements, and has confirmed his old formula $C^{12}H^{12}O^4$ by fresh experiments, some degree of uncertainty must prevail respecting the true formula of leucine.

I have endeavoured to remove these doubts by careful determinations; and I first directed special attention to the obtaining of the substance as pure as possible, as the differences which exist between the analyses of Mulder and those of other chemists, as well as the first and last analyses of Laurent and Gerhardt, could not have arisen with such admirable analytical chemists from errors in the determination, but from a more or less greater impurity of the leucine.

The leucine was prepared according to Bopp's method, by repeated crystallization from water, and purified by boiling with animal charcoal. It was then repeatedly exhausted with boiling alcohol, which removed some other substances besides leucine; so that notwithstanding a considerable quantity was used for the experiment, it was considerably diminished by these operations. Lastly, the residue was recrystallized from hot water.

To determine the equivalent, or rather the number of atoms, of carbon, I employed a combination with oxide of lead, which is easily procured in a pure state, and presents when dry the form of nacreous scales, which scarcely differ in appearance from pure leucine. This compound is obtained when a boiling solution of leucine is mixed with acetate of lead, and ammonia carefully added by drops.

The analysis of this compound, dried over sulphuric acid, furnished 29·3 per cent. of carbon and 46·3 per cent. oxide of lead. Hence it results that 1 equiv. leucine contains 12 equivs. carbon, as according to the preceding determination 11·8 equivs. carbon were found for 1 equiv. oxide of lead.

I then submitted leucine itself to analysis; it was dried at 230°, and burnt with chromate of lead. It furnished—

Carbon	54·4	54·7	12 =	72	54·9
Hydrogen	10·0	10·0	13	13	9·9
Nitrogen	..	..	1	14	
Oxygen	..	..	4	32	

Leucine therefore undoubtedly contains 13 equivs. hydrogen; the formula $C^{12} H^{12} NO^4$ requires only 9·2 per cent. of hydrogen, and it is impossible to obtain in a careful analysis an excess of 0·8 per cent. of hydrogen. The differences which Mulder found in his analyses are certainly owing to an admixture of some other substance; and in fact there is a body which adheres tenaciously to the leucine, and which it appeared to me could be best removed by repeated treatment with hot alcohol.—Liebig's *Annalen*, Oct. 1849.

Gold in Sarawak. *By* C. Grant.

The rains at the beginning of October 1848 fell in great quantities in Sarawak, and a considerable portion of the face of a mountain called Trian was washed down into the plains below.

The deposit was found to abound in gold, and afforded work for fully two thousand men for about a month or six weeks; and it was

reckoned that, at the smallest average, they procured a bunkal a month per man.

The gold was in lumps, and not in dust; and several of the lumps weighed from three to four bunkals, and they were rarely less than one or two amass in weight.

This single fact may, in this locality, lead at some future day to important conclusions; and I am induced to notice it as it corroborates the statements in Mr. Low's work, and at the same time is contrary to the received opinion and the experience of the workings in the Brazils, where gold is rarely to be traced to the neighbouring mountains.—*Journal of the Indian Archipelago*, Oct. 1849.

On the Preparation of pure Titanic Acid. By Prof. WÖHLER.

The author describes the following simple process for the preparation of pure titanic acid.

Finely-pulverized rutile is fused, with twice its weight of carbonate of potash, in a platinum crucible, placed in a clay crucible, the mass reduced to powder, and dissolved in a platinum dish in the requisite quantity of dilute hydrofluoric acid. The very sparingly-soluble, readily-crystallizing potassio-fluoride of titanium described by Berzelius soon begins to separate. The mass is then heated to boiling, with the addition if necessary of more water until the salt has redissolved, and then filtered boiling hot, when glass vessels may be employed if an excess of hydrofluoric acid has been avoided. On cooling, the greater portion of the salt separates in brilliant crystalline scales, so that the liquid congeals to a paste. It is collected on a filter, washed a few times with cold water, pressed between folds of blotting-paper, and purified by recrystallization from boiling water. When dry, it forms a laminar mass, with a mother-of-pearl lustre, resembling cholesterine. From a hot prepared solution in water, caustic ammonia precipitates snow-white titanate of ammonia, which remains perfectly white when treated with sulphuret of ammonium, dissolves very readily in hydrochloric acid, and furnishes pure titanic acid on calcination, with disengagement of ammonia and the characteristic glowing.

The potassio-fluoride of titanium has the remarkable property of not being immediately precipitated by ammonia from a cold solution in water; but when heated, the whole of the titanium is precipitated. This circumstance can be used with advantage to precipitate the iron from the mother-liquor left in the preparation, and to obtain likewise from this perfectly pure titanic acid. The mother-liquor is mixed with dilute ammonia, avoiding an excess; the whole of the peroxide of iron is precipitated with very little titanic acid. The liquid must then be immediately filtered from the iron precipitate, as even at the ordinary temperature the titanic acid begins to separate after some time. The liquid is then heated to boiling, and thus all the titanic acid precipitated as a pure salt of ammonia.

This method is equally applicable to the preparation of pure titanic acid from titaniferous iron. After it has been fused with

carbonate of potash, the mass is dissolved in dilute hydrofluoric acid, when the greater portion of the iron is left undissolved in the state of oxide. When most of the potassio-fluoride of titanium has crystallized out and been purified by recrystallization, the ferruginous mother-liquors are mixed with chlorine-water or a hypochlorite to oxidize the iron, and then treated as above directed.

It is not improbable that this method, on further examination, will prove, with the observance of certain precautions, applicable to the quantitative analyses of the different kinds of titanic iron ores. —*Nachricht. d. Gesells. d. Wissensch. zu Göttingen*, Dec. 1849.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Examination of a new Yellow Colouring Matter. *By* W. Stein.

Towards the end of last year, a new material for dyeing yellow, called *wongshy*, was exported on experiment from Batavia to Hamburg, for a sample of which I am indebted to the kindness of M. Vollsack, merchant. Whether it has hitherto been applied as a dyeing material, and with what results, could not be ascertained. The following notice therefore will probably not be without interest.

The new dyeing material consists of the seed-vessels of a plant, which, according to information from M. Reichenbach, belongs to the family of the Gentianeæ. The form of the unilocular capsules is longish-ovate, drawn out to a point next the end of the peduncle, and crowned upon the opposite and more obtuse one with the dried six-lobed calyx. They vary in size; but on an average their length is 1·5 to 2 inches, and the diameter at the thickest part 0·5; the colour is not uniformly reddish-yellow, but at some places darker, at others lighter. The surface is more or less irregularly waved with six to eight longitudinal ribs. The odour resembles saffron, and subsequently honey. The shell is pretty hard and brittle, but becomes quickly mucilaginous when chewed, imparting a yellow colour to the saliva, with a slightly bitter taste; it swells up considerably in water. Inside the capsules there are a number of dark reddish-yellow seeds (in one specimen I counted 108); they are not attached to the sides, but are imbedded in a hardened pulp, and so connected one with the other. These seeds are tolerably hard, soften but slowly when chewed, have no particular taste, but after some time produce at the point of the tongue a slight but peculiar sourish-sweet pungency, resembling the action of Paraguay rue. The pulp, on the other hand, cementing them together has a strong bitter taste, which is particularly perceptible at the back part of the palate.

The embryo consists of starch-bearing cells, and is surrounded by albumen, as can very readily be shown by iodine, which colours

the embryo throughout blue, but does not change the surrounding mass. Under the microscope it exhibits two cotyledons; it is also seen that the colouring principle is perfectly amorphous, and has in the innermost cells of the seed-envelope a yellow colour with a slight tint of green, whilst in the outer cells it appears purple-red. Starch may be likewise detected by iodine in the shells; and with the microscope we can discover besides the orange- and red-coloured cells, some situated towards the outer margin, the contents of which possess a pale green colour.

The wongshy, especially when pounded, readily gives up to water, both at the usual temperature as well as on boiling, a colouring principle which possesses such an enormous divisibility that 2 parts of the pounded capsules furnish 128 parts of a liquid, which, placed in a cylindrical vessel of white glass with a diameter of three inches, still appears of a bright wine-yellow colour. The concentrated extract is very mucilaginous, and has a fiery red colour, which on large dilution passes into a golden yellow, the red disappearing.

Alcohol, both absolute and of 0·863 spec. grav., when digested with the pounded fruit, acquires a fiery red colour, which on dilution also changes to a golden colour.

When digested with æther at the ordinary temperature, it assumes a wine-yellow or brownish-yellow colour, and leaves on evaporation a thick yellowish-brown oil, which possesses the odour of the fruit, a mild slightly-bitter taste, deposits at 32° a small quantity of a solid fat, and does not become thick when shaken with protonitrate of mercury even after long standing, and consequently belongs to the drying oils. Perfectly colourless fatty acids may be obtained from it by saponification; the colour of the oil is consequently owing to a small quantity of the colouring principle.

Fat oils do not extract any of the pigment from the fruit either at the ordinary temperature or on the application of heat.

The aqueous extract gelatinizes on the addition of alcohol, and the yellowish gelatine may be obtained perfectly colourless by washing with alcohol. It forms when dried a transparent mass, which slowly dissolves in water to a thickish mucilage. In one experiment, in which it was separated from the fermented solution of the colouring principle, it was obtained not as jelly, but in soft flakes, which remained white and opake after drying. It behaved in other respects like the transparent substance. The solution in water is not precipitated by acids; caustic soda produces a gelatinous precipitate only when in excess; added in small quantity the liquid remains clear, but upon the addition of an acid deposits gelatinous flakes. Carbonate of potash acts in a similar manner, with this difference, that an excess causes the liquid to become thick only after a much longer time, and that acids produce but a small flocculent precipitate. The solution is so completely precipitated by barytic water, that the liquid filtered from the precipitate, on evaporation upon platinum and ignition of the residue, does not show any trace of organic matter. Lime-water causes a similar separation, and acetate of lead produces a gelatinous precipitate.

These reactions agree with those of pectine as described by Fremy in his recent investigation.

When the liquid, freed from pectine by means of alcohol, is mixed with a little acetate of copper and a sufficient quantity of caustic soda, and heated to boiling, protoxide of copper separates. There is consequently sugar present, which moreover may be readily detected by forming the pounded fruit into a paste with water, and allowing it to ferment in a moderately warm place.

In this fermentation, which in one experiment was carried on for longer than three weeks, a large amount of carbonic acid was disengaged, and a beer-like odour, which subsequently changed into that of butyric or valerianic acid. On subjecting the fermented liquid to distillation, I obtained a product which contained no alcohol, and only a trace of acetic and butyric acids. I could detect neither lactic acid nor mannite in the residual liquid. This fermentation differs therefore essentially from the so-called mucous fermentation, in which, as is well known, the sugar is decomposed into carbonic acid, gum, lactic acid and mannite, likewise without the production of alcohol.

A solution of gelatine produces in the aqueous extract a trace of a precipitate arising from tannin.

Protochloride of tin produces no change at the ordinary temperature or after a long time; on boiling, a dark orange-coloured precipitate results.

Acetate of lead produces no change.

Basic acetate of lead causes a turbidness at the ordinary temperature, and an orange-coloured precipitate on boiling.

Protosulphate of iron changes the colour into a dark brownish-yellow, without however a precipitate resulting either in the cold or on ebullition.

Alum*, acetate of alumina and acetate of zinc produce yellow precipitates only on boiling.

Barytic water causes a yellow precipitate at the ordinary temperature, which on boiling acquires a reddish tint.

Lime-water gave a pure yellow precipitate; solutions of gypsum and chloride of calcium are not precipitated by it even on boiling; well-water, with a considerable amount of carbonate of lime, does not precipitate the colouring principle even with the assistance of heat; it is consequently not able to decompose the combinations of lime with acids.

Lime and barytic water behave somewhat differently towards the solution of the colouring principle which has been entirely freed from pectine, the precipitates being produced only on ebullition, and in both cases having an orange colour.

Caustic soda, caustic ammonia and carbonate of potash darken the colour and give it a brown tint; this however is not a peculiarity

* The experiments which I made to ascertain whether a beautiful lake colour might be obtained with alum by precipitating with potash did not furnish a satisfactory result, as in fact but little of the colouring material was carried down by the alumina, and this could be entirely removed by washing.

of the colouring matter, but is produced by the action of the alkalies upon the mucilaginous sugar, and a very bitter, readily changeable substance, which I could not isolate. At the same time, on boiling the liquid, when carbonate of potash or caustic soda has been employed, a disengagement of ammonia is perceptible by applying a piece of reddened litmus-paper to the upper part of the vessel.

A small quantity of nitric acid produces no change in the liquid at the ordinary temperature; a large quantity causes the red portion of the colour to disappear, and the liquid is then pale yellow. Each drop of acid produces, as it falls into the liquid, a greenish tint. In this respect it bears a remote resemblance to saffron-yellow, which is coloured green by nitric acid.

Sulphuric acid colours it brownish in the cold; on ebullition the liquid becomes yellowish-green by transmitted, dark green by reflected light; after some time olive-coloured flakes separate, whilst the liquid turns reddish-brown.

Muriatic acid likewise produces no change in the liquid at the ordinary temperature; but on the application of heat, before it begins to boil, it is coloured yellowish-green by transmitted and dark green by reflected light. Dark green flakes soon separate, and the liquid appears reddish-brown. But this reaction, which distinguishes the extract of the wongshy from the solutions of all other known yellow colouring matters, is not produced by the pure colouring principle, but by the previously mentioned bitter substance; and, for this reason, cannot be used to distinguish the wongshy colour when fixed upon cloths, as the bitter substance does not unite with the fibre.

Tartaric and citric acids change the colour to a brown-red. Metallic zinc, on the addition of a few drops of muriatic acid, decolorizes the liquid so far as to render it pale yellow, and the colour is not restored by exposure to the air; woollen fabrics are but faintly coloured by it.

Sulphurous acid and sulphuretted hydrogen likewise effect an imperfect decolorization; complete decolorization can only be attained by the action of chlorine water, and even then with difficulty.

To ascertain the value of the wongshy colouring matter for the purposes of dyeing, 1 part of the pounded capsules was digested for twelve hours with 20 parts of lukewarm water, being frequently stirred, and the liquid then strained. The colouring matter is most quickly extracted in this manner without its becoming gelatinous from the formation of paste, as would happen were the liquid boiled. Properly prepared samples of woollen cloth, some without any mordant, others mordanted with alum, protochloride of tin, acetate of alumina and basic acetate of lead, were dyed with this extract at a temperature of about 104° F.; the colour does not turn out so pure at a higher temperature*. The unmordanted cloth was dyed a beautiful and uniform orange colour by one immersion; of the mordanted samples, those with alum and acetate of alumina were better than with those protochloride of tin; the least satisfactory

* I may here observe that I have not succeeded in preparing a good green from the wongshy yellow.

was that in which basic acetate of lead had been used as mordant. The tone of the colour was not altered by the three first mordants, but it was less intense, and the stuffs were not uniformly penetrated by the colouring matter. However, the samples with alum-mordant gave perfectly satisfactory results after a second immersion. The colouring matter likewise combines readily and uniformly with silk, communicating to it a very glowing golden colour, so that in this case I also prefer not having recourse to mordants. Cotton, as was to be expected, can only be dyed with the assistance of mordants, and the best results appeared to be obtained with tin mordants; the colour was orange, of a very agreeable tint.

The colour, both upon wool, silk and cotton, resists soap perfectly; but alkalies give it a yellow, acids and tin salt a red tint. By this behaviour it differs from the colour of annotto, with which, as will subsequently be seen, it possesses in other respects great resemblance, a resemblance which unfortunately exists as regards the action of light. When exposed to light, the colour very soon fades upon cotton, less quickly upon wool; and in this case it is more permanent upon the unmordanted samples. It resists the light longest upon silk; and in this respect, when compared with the other known yellow colours, may be reckoned among the best.

I obtained a beautiful yellow, with a faint tint of red, by mordanting the woollen cloth with lime-water, and immersion in the boiling vat; it resists the soap perfectly, and the action of light much better than the orange. It is altered in a similar manner to the orange by alkalies, acids and tin salt, only less. Several very beautiful shades of yellow may be obtained by adding pearlash or caustic potash to the dye, and immersing the unmordanted fabric at the ordinary temperature. The union of the colour with the fibre takes place very quickly and very uniformly. By the addition of 1 part pearlash to 30 parts dye liquor, a yellow was obtained with a remarkable glow from a slight admixture of red. By the addition of twice the quantity of pearlash, a lively yellow, with a faint tint of green, was obtained. A still larger amount of pearlash cannot be used, as it renders the colour dull and impure. With caustic potash, instead of pearlash, I obtained in the first place a pure brilliant yellow, with less red than with the pearlash; in the latter case, a beautiful canary-yellow with a shade of green. Ammonia acts in the same manner, but the colour under all circumstances contains more red. The colour also appears of a somewhat different shade when the fabrics are first immersed in the dye liquor, and then, after being washed, placed in an alkaline bath.

In the case of silk and cotton the effect of alkalies is similar, but less apparent, because the silk and cotton fibres imbibe less of the colouring substance than those of wool.

That this colour resists the soap is self-evident, but it also suffers less from the action of light than the orange; and when fabrics so dyed are passed through a vinegar or muriatic acid bath, a brilliant aurora colour is obtained. This interesting behaviour, which the wongshy colouring matter has in common with that of annotto, is explained

by the chemical character of the former, which is a weak acid; it combines with the alkalies and with the alkaline earths, as evident by the precipitation with baryta and lime-water. Its combinations with the former possess a pure yellow colour, and are decomposed by stronger acids, when the liberated colouring matter separates of a brilliant vermilion colour. But the colouring matter thus separated is no longer the same as that which was originally contained in the aqueous solution, for it is now perfectly insoluble in water, and is only dissolved in small quantity, and of a golden-yellow colour, by absolute alcohol, æther and spirit of 0·863 spec. grav. In the moist state it has a vermilion colour; when dry and in the purest state, it is brown-red, like Ratanhia extract, and is easily reduced to powder; but if it still contains sugar and fat, it has a beautiful yellowish-red colour, in thick layers, whilst in thin layers it is yellow and transparent and becomes moist in the air. On heating the pure substance upon platinum, at first yellow vapour is given off, and at some spots the colour becomes pure yellow; it subsequently turns black, fuses and chars. The residual cinder is difficult to burn; the yellow vapours condense, when the experiment is made in a glass tube, into yellow oily drops. Concentrated sulphuric acid renders it scarcely perceptibly blue, and the acid acquires the same colour, which quickly passes into violet and brownish-red, whilst the colouring matter slowly dissolves. Water separates from this solution a dirty yellowish-gray flocculent substance.

The reaction of the wongshy colouring matter, which has just been mentioned, has no resemblance with the reaction of sulphuric acid upon annotto, for the liquid never acquires a pure blue colour, as is the case with annotto, but is violet from the first, and only for a minute.

It dissolves readily in caustic ammonia and caustic soda with a golden-yellow colour.

To obtain it in a pure state, the extract of the pounded wongshy capsules obtained with absolute alcohol must be separated by distillation from the alcohol, the residue treated with æther to free it from fat, then dissolved in water, and the solution precipitated by acetate of lead and the addition of ammonia. The well-washed lead precipitate is suspended in water, and decomposed with sulphuretted hydrogen.

When the liquid separated from the sulphuret of lead is heated with muriatic acid, it acquires a green colour; and if evaporated, only a small quantity of a brown substance, no longer soluble in water, is obtained. This is evidently a product of decomposition of the above-mentioned bitter substance, the greater part of which however is removed by the æther along with the fat*. When the dried sulphuret of lead is now treated with absolute alcohol, the latter

* To obtain this pure from the ætherial solution, I dissipated the æther, treated the residue with water, in which, to separate the fat, I dissolved some chloride of sodium; the fat was removed by filtration, the residue exhausted with alcohol, the liquid evaporated at 124°. On evaporating the alcohol, I obtained a brown, no longer bitter residue, which likewise was no longer soluble in water.

acquires a yellow colour, and leaves on evaporation* the cinnabar-red colouring substance. The produce however was so small that I was unfortunately not able to submit it to elementary analysis. With Levol's test I could discover no nitrogen, and by boiling with caustic potash no sulphur. The insolubility of the colouring principle in water, after its separation from combination with the basic oxides, in opposition to its ready solubility in it before it had been combined with bases, induced me to make some experiments for the purpose of explaining this peculiarity. That neither the sugar nor the pectine could cause the solubility of the colouring matter was proved, on the one hand, from the circumstance that the colouring substance was separated by vinegar from a solution which still contained sugar after it had been boiled with caustic soda, and that the pure substance was neither soluble in a solution of pure pectine nor in one mixed with sugar. I was however surprised to find that the separation by acids resulted immediately only after the watery solution of the colouring matter had been boiled with caustic soda, and that it required a much longer time at the ordinary temperature. From this I concluded that the colouring matter must originally occur in the state of a combination, which is completely decomposed by ebullition with caustic soda. I imagined it to be an ammoniacal compound, since, as previously mentioned, I had observed a disengagement of ammonia on boiling with caustic soda. But this disengagement was scarcely perceptible at the ordinary temperature, and no ammonio-chloride of platinum was formed by the addition of chloride of platinum even on evaporating the liquid. This appears to justify the view that the wongshy colouring principle is an amidogen compound; and this view is moreover supported by the fact, that the colouring substance, after boiling the solution with caustic ammonia, cannot be separated by acids, whilst it was separated from the aqueous solution which still contained sugar on ebullition with muriatic acid, not it is true with its vermilion colour, but brownish-yellow, owing undoubtedly to its being mixed with the products of decomposition of the sugar.

The final decision of this question by elementary analysis of the soluble, as also of the insoluble colouring matter, was impossible for want of material. I hope however to return soon to the subject.

I have stated that the wongshy capsules contained 5 per cent. of ash. They were readily burnt at a gentle heat in the pounded state, and very perfectly when previously mixed with platinum powder. I constantly observed, in some experiments in which no platinum was employed, at a certain temperature, a sudden and lively combustion, which led me to imagine that the fruit might perhaps contain nitre. I therefore exhausted the mass, which had been completely deprived of colouring matter by absolute alcohol, with water, and tried to detect nitric acid in this extract by protosulphate of iron; I also heated another portion with sulphuric acid,

* On one occasion I observed with the assistance of a lens some white acicular crystals with the amorphous colouring matter in the solution concentrated by evaporation.

but in both cases not a trace could be found. The ash of the wongshy capsules becomes readily moist, and effervesces strongly with acids. It was saturated with nitric acid, and the phosphoric acid determined by means of mercury according to Rose's method, and the other constituents according to the usual methods. 100 parts of ash furnished—

Phosphoric acid	10·27	= 5·75 O
Silica	4·00	
Sulphuric acid	0·93	
Chlorine	0·55	
Lime	11·96	= 3·36 O
Magnesia	3·47	
Peroxide of iron	5·51	
Soda	11·35	
Potash	29·19	
	77·23	

The solution of the ash, neutralized with nitric acid, gave a beautiful yellow precipitate with nitrate of silver; and the amount of oxygen contained in the lime is to that in the phosphoric acid in the same proportion as in a basic phosphate of lime of the formula $3CaO, PO^5$. Whether the two substances are really combined in this manner, I must leave undetermined, as it has been satisfactorily shown by Rose's investigations how little we are at present justified in drawing conclusions as to the state of combination of the inorganic constituents of plants from the results of ash analyses. The largest amount of the basic oxides above enumerated must have been combined with vegetable acids in the fruit, as they were united with carbonic acid in the ash. The quantity of the latter amounts to 21·67 per cent. when the alkalies are viewed as carbonates, and the loss of 1·10 per cent. is undoubtedly to be considered as carbonic acid combined with the magnesia, which, on incineration in the presence of alkaline carbonates, is only imperfectly separated from the magnesia.—*Journ. für Prakt. Chem.*, Dec. 1, 1849.

Experiments relative to the Temperature at which Gun-Cotton explodes. By Dr. C. Marx.

The author communicates a series of experiments relative to the temperature at which gun-cotton explodes. It results from these that it goes off even at 144° F., but on an average at 199°, when raised to this temperature from that of the air, within five minutes. Further, that it does not explode when heated so slowly that the temperature is not increased more than 5° F. per minute, but begins to be slowly decomposed at 131°, and its explosive force is very much weakened with the progress of the decomposition. This circumstance deserves attention in respect to the conveyance of explosive cotton, as metallic objects readily acquire a temperature of 144° by exposure to the sun.—Poggendorff's *Annalen*, lxxviii. p. 101.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Atomic Weight of Mannite, and on Explosive Mannite. *By* Dr. W. Knop.

Some years ago I published, in conjunction with M. Schnedermann, some experiments on sulpho-mannitic acid. Favre had made known a little earlier an investigation on the same subject, which came to our knowledge when our paper had already been printed off for Liebig's 'Annalen.'

It was known at that period, from the analyses of Liebig and Pelouze, that mannite was removed from the series of the true sugars by its amount of hydrogen, which is certainly more than required to constitute with the oxygen of the mannite precisely that relation in which these two elements form water. The simplest atomic relation has been expressed by Liebig and Pelouze by $C^6 H^7 O^6$.

The first experiments to determine the equivalent of mannite, those of Favre on the one hand, and of Schnedermann and Knop on the other, were directly opposed. Favre assigned to mannite the formula $C^6 H^7 O^6$, whilst according to our experiments the formula $C^8 H^9 O^8$ agreed better with the facts. The first formula has been generally admitted; some chemists however have adopted the formula $C^{12} H^{14} O^{12}$, which is derived from Favre's by doubling it, and would also be obtained from the composition found by us for the sulpho-mannitates if the composition $3RO + 6SO^3$, $C^{12} H^{11} O^9$ be admitted.

Favre has stated, that on bringing together a hot ammoniacal solution of acetate of lead with a concentrated solution of mannite, a crystalline compound with oxide of lead is obtained by cooling, or by precipitating with alcohol. Favre has moreover asserted, that his sulpho-mannitate of lead may be obtained by dissolving mannite in sulphuric acid, neutralizing with chalk, decomposing the filtered solution with acetate of baryta, and precipitating the lime-salt so obtained with basic acetate of lead. The composition of the above-named compounds is said to be—

Mannite-oxide of lead....	$2PbO, C^6 H^5 O^4$
— — —	$3PbO, C^6 H^5 O^4$
Sulpho-mannitate of lead..	$4PbO + 2SO^3, C^6 H^5 O^4$

I have long ago repeated these experiments of Favre, and given myself much trouble to produce some combination with mannite from which its atomic weight might be safely calculated. The result of all these experiments may be thus expressed:—Excepting the compound with nitric acid, no combination of mannite exists from which a satisfactory determination of this point can be expected. I have from time to time examined with this view all the ordinary acids, and have obtained but one single compound, that with formic acid, which in any way bears the character of a true combination. Experiments with bases were just as unfavourable; they either do not act upon the mannite, or products of decomposition are obtained at higher temperatures of such nature that no conclusion can be drawn from them even as to the composition of mannite.

With respect to the experiments of Favre, I am not able to explain how the analyses of the above three different compounds agree so well with the formulæ. It is possible that I did not succeed in obtaining the same compounds, yet I must observe that I repeated the experiments frequently, and each time obtained products which were readily perceived to be mere mixtures of the components.

I have also again examined the sulpho-mannitic acid. As no good result was to be expected from the plan formerly pursued, since the salts do not crystallize and we have no safe criterion as to purity and the absence of mixtures, I now saturated the acid with carbonate of baryta, and evaporated only a portion of it to dryness. I. Substance from two different preparations left, after being long dried at 149° F., in one case 46·0, in the other 45·05 per cent. of sulphate of baryta. II. Another portion of the same liquid was precipitated with absolute alcohol. The salt obtained left, after calcination and repeated moistening with concentrated sulphuric acid, 49·7 per cent. sulphate of baryta. III. The filtered alcoholic liquid still furnished a residue, which on combustion left 25·8 per cent. sulphate of baryta. I analysed the salt II.; 0·6225 of the salt, dried at about 122° over sulphuric acid, furnished 0·332 carbonic acid and 0·140 water. Further: 0·78 grm. of the same salt gave 0·3876 sulphate of baryta. These numbers correspond with 49·7 BaO, SO^3=66·7 BaO, $2SO^3$, 14·56 carbon and 2·4 hydrogen, and admit of no formula being deduced. In like manner the results of I. and II. show that the combination of sulpho-mannitic acid in the above treatment either consisted originally of a mixture, or was decomposed into one during the treatment. It is therefore very probable that the salt formerly described by us was a mixture.

It is evident from these facts that the data for the determination of the atomic weight are not satisfactory. For this reason I have made numerous other experiments, but only the results which were obtained with the formiate of mannite deserve to be mentioned; and even this compound has such unfavourable properties, that it is not brought forward as deciding the formula and the atomic weight. However, the analyses point to the original formula of Liebig and Pelouze, $C^6 H^7 O^6$.

Formiate of Baryta.—When crystallized oxalic acid and mannite

are fused together in an air-bath at 230°, and the temperature is then allowed gradually to sink to 212°–204°, there is obtained after six or eight hours a perfectly transparent and almost colourless or somewhat yellowish syrup, which on cooling becomes tolerably solid, remaining transparent. During the whole operation formic acid and carbonic acid are disengaged; and it appears that the oxalic acid is more readily decomposed under these circumstances into these products than alone. The mass dissolves in alcohol of 0·833 (in which mannite is scarcely soluble) pretty readily, and is soon decomposed in this solution into mannite and formic acid. According as a greater or smaller excess of oxalic acid was used or the temperature was raised, oxalic acid is left behind on solution in alcohol. If the compound has towards the end been retained for several hours at 204°, oxalic acid being present in excess, the odour of formic acid on cooling is very faint. When placed over sulphuric acid, it loses in the course of several days its transparency, and the odour of formic acid becomes very strong. From this it appears that this substance is in reality a compound of formic acid with mannite, which is however readily decomposed.

In every experiment where the compound was brought into contact with bases, it was decomposed into mannite and a salt of formic acid. The following are the experiments:—

I. The filtered solution in strong alcohol, on being mixed with an alcoholic solution of potash, deposited a substance which left on calcination 3 per cent. of carbonate of potash, and was not therefore further examined.

II. The solution in strong alcohol was poured into water, supersaturated with barytic water, left for a long time over sulphuric acid under a bell-glass—during which time there was a constant disengagement of carbonic acid—filtered from carbonate and oxalate of baryta, and was, when concentrated and perfectly neutral, precipitated with alcohol; it became turbid, and deposited a viscous mass. The filtered liquid deposited in the course of twelve hours crystals which consisted of uncombined mannite with formiate of baryta; the mixture contained 27·55 per cent. carbon, 5·03 hydrogen, and 26·59 baryta.

III. Exactly similar results were obtained on saturating with lime and oxide of zinc, when the solutions were subsequently precipitated with alcohol. As it was perfectly evident from these experiments that the combination does not saturate bases like that with sulphuric acid, the compound was treated in such a manner that the quantities of mannite and formic acid which are set free on the decomposition of the compound could be determined.

1. Mannite was kept with a large excess of crystallized oxalic acid for five hours at 230°, and then for four hours more at 203° in order to remove all free formic acid as much as possible. There was still some undecomposed oxalic acid present; the solution precipitated salts of lime. The fused mass was spread out in a shallow dish, and rinsed two or three times with æther to remove any formic acid, then dissolved in water, accurately saturated with lime, and

lastly with lime-water. After some time the previously perfectly neutral solution again exhibited a very faint acid reaction, so that it appears as if a small amount of formic acid is liberated at a later period. A portion was supersaturated with lime-water, the excess of lime removed by carbonic acid, the liquid heated, filtered and evaporated. 0·5775 of the residue, dried at 230°, gave 0·2425 sulphate of lime =0·0098, or 17·2 per cent. lime. 0·7835 of the same substance, dried at 230°, furnished 0·813 carbonic acid and 0·361 water =0·2217 carbon and 0·0401 hydrogen, including the carbonic acid which remained with the carbonate of lime; we obtain from this the following numbers, which are compared with $C^6 H^7 O^6 + C^2 HO^3, CaO$:—

Carbon	31·94	8 =	48	30·8
Hydrogen	5·12	8	8	5·1
Oxygen	45·74	9	72	46·2
Lime	17·20	1	28	17·9

The salt was burned upon a long strip of platinum in oxygen gas, and the products of the combustion passed through a tube about a foot in length filled with coarse oxide of copper. The residue of lime had parted with some carbonic acid, and turned litmus-paper blue; the analysis therefore must contain an excess of carbonic acid.

2. Mannite, treated as before, the fused mass spread out while warm upon a shallow dish, rinsed after cooling with æther, and then digested for some time with recently precipitated carbonate of zinc, filtered and evaporated to dryness, showed a loss on drying at 230° in twelve successive weighings, and appeared to be partially decomposed. The substance thus treated was therefore dried at a gentle heat for four days over sulphuric acid, and then burned on a long strip of platinum in oxygen; in front of the combustion-tube was placed a long column of coarse-grained oxide of copper; 0·3133 substance, calcined in a crucible, gave 0·0685 oxide of zinc =21·8 per cent. 0·645 substance gave 0·676 carbonic acid and 0·2975 water. The oxide of zinc, towards the termination of the combustion, was heated to a bright red in the tube; there was left 0·144 upon the slip of platinum, from which no carbonic acid was disengaged on solution in acid. These numbers correspond to 21·8 and 22·32 oxide of zinc, 28·58 carbon and 5·12 hydrogen. Comparing these results with the expression $C^6 H^7 O^6, C^2 HO^3 + ZnO, HO$, we obtain—

Carbon	28·58	8 =	48	27·22
Hydrogen	5·12	9	9	5·08
Oxygen	..	10	80	
Oxide of zinc	22·32	1	40	22·60

With respect to these analyses, the hydrogen may be looked upon as exceedingly accurate. Indeed both the analyses were made with such care, that they may certainly be considered to express the constitution of the substances in question; and I think that if a mixture of mannite and a salt of formic acid were dissolved, filtered from excess of base and treated as above described, it would not be

easy to obtain results agreeing more closely with the formula, supposing the formula of mannite to be really $C^6 H^7 O^6$.

3. Lastly, the mass obtained by fusing mannite with oxalic acid was treated in the same manner as 1 and 2, and saturated with barytic water. It was quite evident in this case that the solution accurately saturated with barytic water frequently again became faintly acid, pointing to a gradual decomposition of the compound. I obtained from 0·2825 dried substance, 0·158 sulphate of baryta =36·81 baryta. Supposing this mixture, which had been kept for three weeks at a gentle heat over sulphuric acid, to be $C^6 H^7 O^6 + BaO, C^2 HO^3$, theory would require 37·0 per cent. of baryta.

These experiments I made three years ago, but did not publish them, hoping to obtain some more constant compound. Since then such a compound has been described. The combination of nitric acid with mannite of Flores Domonte and Ménard, so far as I have examined it, appears well suited to decide in what proportion the number of atoms of carbon enter into combination with other bodies. As yet no results of the analyses of explosive mannite have been published. Stenhouse, in his last investigation on the lichens, mentions explosive mannite, and assigns to it the formula $C^{12} H^{9} O^{7} + 5NO^5$. Reinsch has recently stated that explosive mannite, on being decomposed with potash, furnishes an alkaloid; all else that is known of this substance relates principally to its preparation. I will now describe some experiments made with some of the products of decomposition of this substance.

Explosive Mannite.—Of all the methods for preparing this substance, Stenhouse's is the best. Mannite is dissolved in fuming nitric acid, which is kept very cold, in the proportion of $\frac{1}{2}$ an oz. of mannite to 2 oz. of acid; after a few minutes cold sulphuric acid is added, whilst the mass is placed in cold water until no more white flakes or grains separate. In this manner we apparently obtain nearly the whole amount of the mannite converted into explosive mannite. As soon as the separation has resulted, the cold mixture is poured into a large quantity of water. Sulphuric acid must no longer be added after separation has taken place, otherwise the product again dissolves. If the crude product is dissolved in boiling alcohol, and this solution is then poured into a large quantity of cold water, it becomes turbid, and in the course of twelve hours the mannite cakes together, and may be readily filtered and washed.

The product thus obtained dissolves readily in boiling alcohol, and crystallizes from it for the greater part on cooling. Sulphuretted hydrogen has no action upon this solution; the solution of the crude product containing nitric acid, deposits some sulphur until the nitric acid is destroyed. Sulphurous acid has apparently no action upon it.

Metals, as zinc, copper and iron, decompose explosive mannite when dissolved in alcohol, iron very readily. All these metals effect the decomposition more rapidly when muriatic acid or chloride of ammonium are added.

1 oz. of explosive mannite dissolved in 8 to 10 oz. of alcohol was digested for eight days in a flask loosely filled with iron shavings, and frequently heated to boiling; it was entirely decomposed. The bottom of the vessel was covered with a thick layer of peroxide of iron. The almost colourless slightly yellowish liquid, which during this treatment was constantly renewed, left on filtration and evaporation half a gramme of an ammoniacal salt. One half of the peroxide of iron, on being exhausted with sulphuret of ammonium furnished a brown liquid, which gave one gramme of a crystalline mixture of an ammoniacal salt with one of a volatile organic acid, with which some mannite appeared to be mixed. The other half of the peroxide of iron was exhausted with carbonate of potash; it furnished a dark brown liquid, in which a few crystals likewise formed, but they could not be separated sufficiently from the brown mass to be determined more accurately. The whole quantity did not amount to 1 gramme. Consequently explosive mannite must be converted by iron for the greater part into gaseous products, which on boiling the alcoholic solution are seen to ascend from the iron even after the fire has been removed from the flask and no more alcoholic vapour escapes in bubbles. In this operation, so long as there is much explosive mannite present, the odour of an æther of a volatile acid is perceptible.

This decomposition goes on rapidly when the solution of explosive mannite in æther is filled with iron turnings, and then absolute alcohol mixed with concentrated hydrochloric acid added to it. The liquid becomes heated, turns green, then greenish-black (deutoxide of nitrogen and protochloride of iron) with a violent disengagement of gas. The collected gas shaken with lime-water renders it turbid, and turns quite red on access of the air. Nitric oxide is contained in abundance in the gas.

Metals act in the same manner on solutions of explosive sugar and collodion, at least when muriatic acid is added, as on the alcoholic solution of explosive mannite in alcohol. The products which are produced in this case, or by other reducing agents, as FeO, SO^3 and Sn Cl, I shall describe on some future occasion.

Other products of decomposition are formed when explosive mannite is treated with alkalies; with potash it gives brown products which are not of such a simple nature as to allow of any conclusion being deduced from them as to the constitution of mannite. As Reinsch has stated it to be his intention to examine these products, I have not devoted any attention to them. When explosive mannite is heated alone, it melts and again solidifies to a crystalline mass. By heating very cautiously small quantities in a brisk current of hydrogen, a portion of the acid can be expelled, and the gas which comes over is strongly acid.

The facts which I have described show that—1st, explosive mannite is the only compound of mannite of sufficiently constant nature to assist in determining the atomic weight of mannite. If therefore the formula $C^{12}H^9O^7+5NO^5$, which Stenhouse has adopted for explosive mannite in his last paper on the lichens, is deduced from

accurate analyses, there can be no doubt that mannite has the formula $C^{12} H^{14} O^{12}$. 2nd. Mannite forms a compound with formic acid, when fused at a temperature of from 212° to 230° with oxalic acid. 3rd. The lead compounds described by Favre are mixtures and not salts; they certainly cannot be used in determining the equivalent of mannite, since Favre analysed the crystals which separated on the addition of a concentrated solution of mannite to a hot ammoniacal solution of acetate of lead, after drying them merely between blotting paper, as they could not be washed. The property of the supposed mannite compound of turning yellow at 266°, agrees very well with that of a basic acetate of lead. 4th. That the precipitate which alcohol produces in an ammoniacal solution of acetate of lead, mixed with mannite, after washing with boiling water, is also a mannite compound with the formula $2PbO, C^6 H^5 O^4$, is quite incorrect. With respect to the compounds of sulpho-mannitic acid, which were first examined by Schnedermann and myself, it is possible that they were mere mixtures, as the salts did not crystallize but were merely evaporated to dryness. It appears however to me, that we shall be better able to form an opinion of these compounds, as also of those with formic acid, when the analyses of explosive mannite shall have been repeated.—*Pharm. Central Blatt., Nov.* 28, 1849.

On the Presence of Sugar of Milk in the Cotyledons of the Seed of Vegetables. By H. Braconnot.

The presence of sugar of milk in the cotyledons of seeds is a fact which in my opinion may give rise to very important physiological considerations. Hitherto this singular substance was thought to be formed only by a special organ of the higher animals; it appears however that M. Winckler has detected its presence in the eggs of birds. It could hardly be expected to be found in the fleshy lobes of the seed, where it appears to act an important part, as one of the essential principles of the milk intended for the nourishment of the embryo in that period of vegetable life which corresponds to the lactation of the Mammalia or to the incubation of birds. Eggs moreover have a singular relation with seeds, inasmuch as it appears that their chemical functions are identical. Long since anatomists had noticed that the embryo is connected with the lobes or cotyledons, and there distribute a multitude of ramifications, which have been very properly called mammary vessels, because they pour into the body of the radicle the milky liquid prepared by the hands of nature to effect the first development. It is with equal justice that the same observers have compared to mammæ these cotyledons where the embryo sleeps as in a kind of cradle.

I believe I have satisfactorily demonstrated that the cotyledons of the acorn contain all the elements of milk, as we not merely find there milk-sugar, but likewise a considerable amount of caseous matter, a slightly nitrogenous extractive substance, a large proportion of phosphate of lime, as also the soluble salts which occur in milk; and lastly a fatty substance, which however does not possess

the consistence of butter; but this, as is well known, varies even in the milk of the same animal.

With respect to other seeds, especially those with fleshy cotyledons, as peas, beans, &c., I have every reason to believe that milk-sugar will be found in them when directly sought for. Under certain circumstances, however, the substance crystallizes only with great difficulty and after a long time; it is probably owing to these circumstances that it had hitherto been found only in the milk of the Mammalia, where it is far more easy to free it from foreign matters.—*Ann. de Chim.*, Dec. 1849.

Examination of the Liquid from a Case of Ovarian Dropsy.
By Thornton J. Herapath, *Bristol**.

For the specimen of fluid which I have examined, I am indebted to my brother, Dr. William Bird Herapath, who removed it, on the 22nd of last November, by paracentesis abdominis, from the cavity of the ovarian cyst of a female patient. The quantity so obtained amounted to about five and a half gallons.

It was of a light reddish-brown colour, somewhat viscid, and frothed when agitated. It possessed a rather unpleasant odour, and a slightly salt taste. The specific gravity at 61° F. was 1·011. It exerted a very marked alkaline reaction on turmeric, and reddened litmus-paper, from the presence of carbonate of soda or potash. Under the microscope there were exhibited a few corpuscles, which were somewhat similar in appearance to blood-discs, but more granulated. They were most probably imperfect, or perhaps altered blood-globules. No pus could be detected.

When allowed to remain undisturbed for a short time, a thin web of fibrine was gradually deposited. On being heated, it became opake, and finally transformed into a thick tremulous mass, from the coagulation of the albumen. The same effects were produced by the addition either of sulphuric, hydrochloric or nitric acid, especially with the latter. Acetic acid caused a slight precipitate, which was insoluble in excess; and this was greatly increased upon the further addition of ferrocyanide of potassium. Infusion of galls occasioned a bulky grayish precipitate, which was not redissolved upon boiling. In the fresh liquid, bichloride of mercury produced an abundant precipitate; but after boiling and filtering, it was but slightly affected by this reagent. Heated with a few drops of a solution of potash or soda, it gave off a very evident ammoniacal smell, arising from the decomposition of the urea. On incinerating the dried residue that remained after evaporation, an ash was obtained which was almost entirely soluble in water. The solution was highly alkaline, from the presence of carbonate of soda; it likewise contained chlorine and small quantities of phosphoric and sulphuric acids with potash. The insoluble salts were chiefly composed of the carbonates and phosphates of lime and magnesia, with a minute proportion of perphosphate of iron and silica.

* Communicated by the Author.

I. *Quantitative Proximate Analysis.*

1106·04 grs. of the fresh liquid were carefully evaporated to dryness at a steam-heat; the residue weighed 37·24 grs. This was then repeatedly extracted with a boiling mixture of alcohol and æther; the residue again dried, &c., and the loss noted; it amounted to 5·63 grs.

The alcoholic solution was evaporated to dryness, and treated several times successively with boiling æther, which removed 0·565 gr. of fatty matters and lactates or lactic acid. The presence of lactic acid in this solution was proved by again evaporating to dryness, redissolving in water, and boiling the aqueous solution thus obtained with oxide of zinc, when by concentration a salt was obtained which was perfectly similar in character to the lactate of zinc prepared from muscular flesh*.

That portion of the alcoholic extract which was insoluble in æther was principally composed of urea and a peculiar extractive matter, mixed with a small quantity (0·21 gr.) of inorganic salts (chloride of sodium principally, with a little carbonate of soda and phosphate of potash).

The substances that were left undissolved by the boiling alcohol were then reduced to a fine powder, and repeatedly treated with boiling water. This menstruum extracted the gelatine and mucus(?) together with the residuary soluble inorganic salts. This aqueous solution was not rendered turbid either by boiling or the addition of nitric acid; but it nevertheless contained albumen in combination with soda†. To estimate the former, the solution was concentrated to the consistence of a syrup, and connected by means of two platinum electrodes with a small galvanic battery, when the albuminate of soda was decomposed, and the albumen attracted by the positive pole, whence it was carefully detached and weighed. The residuary matters were afterwards incinerated, and the weight of ash noted; it amounted to 8·42 grs.

The insoluble albuminous residue, after extraction by water, alcohol and æther, was found to weigh 22·380 grs., and when burnt left 0·44 gr. of an ash composed of the earthy phosphates and carbonates.

In order to determine the true amount of urea contained in this liquid, I had recourse to a modification of Lassaigne's process, which I have already described in a paper on the examination of the choleraic fluids‡. 1106·04 grs. gave 8·875 grs. of pernitrate of urea =4·656 grs. of urea.

* 2·99 grs. of the salt, dried at 212° F., gave 0·998 gr. of oxide of zinc =33·38 per cent. This agrees very well with the composition attributed by Dr. Heintz to the combination of oxide of zinc with the lactic acid of muscular flesh, viz. $C^6H^5O^5$, ZnO+2HO, which would require 33·33 per cent. of ZnO. Unfortunately want of material prevented me from further establishing their identity by an ultimate analysis.

† The same remarks, I may observe, have been made by Dr. Wright with regard to the salivary juices. Indeed it was from the perusal of that gentleman's paper on this subject that the idea was first suggested to my mind of decomposing the albuminate of soda by means of galvanism.

‡ Medical Gazette, No. 1146, Nov. 16, 1849.

I likewise succeeded in detecting the presence of an exceedingly small proportion of uric acid, but the quantity was too minute to be estimated. No kreatinine, sugar or succinic acid could be discovered. I was induced to look for the latter in consequence of the publication of a paper by Dr. W. Heintz*, in which that chemist states that he has detected succinate of soda to the amount of nearly 0·5 per cent. in the liquid of hydatid cysts, which he examined, from the liver of a woman.

II. *Inorganic Constituents.*

The dried matters resulting from the evaporation of a similar quantity (1106·04 grs.) of the fluid were incinerated, with the necessary precautions, in a covered platinum crucible; they left 9·29 grs. of ashes. Of these water extracted 8·60 grs., which, when analysed by the ordinary methods, gave of—

	grs.
Carbonic acid	0·4400
Sulphate of barytes, 0·02 gr. $=SO^3$	0·0067
Phosphoric acid	0·2774
Chloride of silver, 16·46 grs. $=Cl$	4·1150
Mixed chlorides of potassium and sodium	8·644
Potassio-chloride of platinum, 1·634 gr. $=KaCl$	0·5866
Chloride of sodium (by loss)	8·0580

quantities which are equivalent to—

Carbonate of soda	1·0800
Sulphate of potash	0·0147
Phosphate of potash, $2KaO, PO^5$	0·6473
Chloride of sodium	6·8580

The insoluble salts weighed 0·69 gr., and furnished of—

	gr.
Carbonic acid	0·062
Sulphuric acid	traces
Phosphoric acid	0·166†
Phosphates of iron and alumina	slight traces
Silica	slight traces
Carbonate of lime, 0·605 $=CaO$	0·374
Pyrophosphate of magnesia, 0·060 $=MgO$	0·024
Carbonaceous matters	0·200

that is to say of—

Carbonate of lime	0·0800
Carbonate of magnesia	0·0500
Phosphate of lime, $3CaO, PO^5$	0·3600
Phosphates of iron and alumina	traces
Sulphate of lime	traces
Silica	traces
Carbonaceous matters	0·2000

* Jenaische Annalen für Physiologie und Medecin.

† This was estimated by precipitating the acetic acid solution of the earthy phosphates by subacetate of lead, and decomposing the phosphate of lead so produced by sulphuric acid. The numbers were as follows:—$3PbO, PO^5$, 0·913 gr. gave of PbO, SO^3, 1·023 gr. $=PbO$ 0·747. Therefore 0·913 minus 0·747 $=0·166$ PO^5.

From these experiments therefore it appears that 1106·04 grs. of this fluid contained of—

		per 1000 grs.
Fibrine	0·9980	= 0·9024
Albumen	21·9400	19·8372
Fatty matters and lactic acid, or alkaline lactates	0·5650	0·5108
Urea	4·6560	4·2027
Uric acid	traces	traces
Extractive matters, soluble in alcohol but insoluble in æther	0·1990	0·1798
Gelatine, with some mucus and extractive matters	0·4871	0·4404
Albumen, with soda	0·3229	0·2919
Ash: Carbonate of soda	1·0800	0·9764
Ash: Sulphate of potash	0·0147	0·0132
Ash: Phosphate of potash, $2KaO, PO^5$	0·6473	0·5852
Ash: Chloride of sodium	6·8580	6·2008
Ash: Carbonate of lime	0·0800	0·0723
Ash: Carbonate of magnesia	0·0500	0·0452
Ash: Phosphate of lime, $3CaO, PO^5$	0·3600	0·3254
Ash: Phosphates of iron and alumina	traces	
Ash: Sulphate of lime	traces	
Ash: Silica	traces	
Water and loss	1067·7820	965·4093
	1106·0400	1000·0000

On the various Modifications of Metaphosphoric Acid.
By M. Fleitmann.

Some time ago Fleitmann and Henneberg showed, that besides the *a*-, *b*- and *c*-phosphoric acids, which are admitted on the authority of Graham, four similar modifications have to be distinguished. It was possible to arrange two of these modifications immediately as intermediate members in Graham's series; but the other two have the same capacity of saturation as metaphosphoric acid, so that they had to be regarded as distinct acids.

This investigation, which was commenced in Giessen, has been continued by M. Fleitmann in H. Rose's laboratory in Berlin, and the following new results obtained.

When ordinary phosphoric acid is heated with an equivalent of soda until the basic water is expelled, it depends on the mode of heating which of the three modifications of the metaphosphoric acid arranged by Fleitmann and Henneberg side by side as distinct acids shall be formed. When the mixture is fused and quickly cooled, the ordinary uncrystallizable deliquescent metaphosphate of soda is formed. The soluble crystalline salt of Fleitmann and Henneberg is formed with the preceding salt when the fused mixture is allowed to cool very gradually. The third modification, the soda compound of which is perfectly insoluble in water

and dilute acids, is produced when the mixture is merely heated to 572° F. and not fused.

Phosphoric acid behaves very differently when it is heated or fused with any other base instead of soda; for whilst but few bases are capable of taking the place of the soda in forming the one or other of the known modifications of metaphosphoric acid, other bases, on being fused with phosphoric acid, give rise to the production of new modifications.

The compounds which are obtained on fusing phosphoric acid with the other bases, are all perfectly insoluble in water and in dilute acids. The plan which the author adopted for investigating the acids contained in these compounds was in general by decomposing the insoluble metallic compounds by treatment with soluble alkaline compounds, and so transferring the acid to other bases. When the properties of the compound rendered this impossible, no certain information could be obtained as to the nature of the acids.

The insoluble crystalline copper compound which is produced on melting oxide of copper with excess of phosphoric acid, forms the starting-point of these experiments. This salt contains a new well-characterized acid, which forms readily-soluble compounds with the acids, and sparingly-soluble salts with the other metallic oxides, all of which crystallize well. The acid is remarkably stable.

The combinations of the acid with potash, soda and oxide of ammonium are obtained from the finely-pulverized copper salt by decomposition with solutions of the hydrosulphates of the above bases. The potash salt crystallizes with 2, the soda salt with 4 equivs. of water. The ammonia salt is anhydrous. The sparingly-soluble combinations with the other metallic oxides are obtained by decomposing the respective soluble compounds of these bases with solutions of the alkaline salts of the acid. The lead and silver salts crystallize anhydrous; the copper and zinc salts contain 8 equivs. water.

The salts of the acid differ from the crystalline salts of the former modification of metaphosphoric acid discovered by Fleitmann and Henneberg by being far less soluble; but the different proportion in which the salts enter into double compounds with each other constitutes the most essential difference.

The double salts of the acid discovered by Fleitmann and Henneberg constantly possess such a composition that 2 atoms of the one salt is united with 1 atom of the other salt. From this relation Fleitmann and Henneberg deduced the rational formula $3PO^5 + 3HO$ for the acid.

The salts of Fleitmann's new acid always combine, on the contrary, in the same number of equivalents to double salts. In accordance with this, Fleitmann gives to the acid the rational formula $2PO^5 + 2HO$, in order to distinguish it from the preceding.

The same acid which is obtained by heating phosphoric acid with oxide of copper is likewise formed by the action of the isomorphous bases, oxide of zinc and protoxide of manganese. All the other bases with which Fleitmann succeeded in ascertaining the nature of

the compounds produced, furnish, when heated with phosphoric acid, different acids.

The oxide of lead, oxide of bismuth and oxide of cadmium yield, on being fused with phosphoric acid, crystalline compounds, which contain a second metaphosphoric acid. The soluble salts of this acid, which were obtained from the insoluble salts in the same manner as in the case of the previous acid, are perfectly amorphous. The soda salt forms a mass resembling caoutchouc. The nature of the salts did not allow of the preparation of double compounds, so that no information could be obtained in this respect as to the constitution of the acid. The author however observed that the same acid is produced when phosphoric acid is heated with a mixture of equivalents of oxide of copper and soda, instead of with one of the bases above mentioned. The perfectly insoluble double salt of the acid thus formed obtains from its composition the formula $CuO+NaO+2PO^5$, according to which the acid in it appears to contest the same rational formula with the oxide of copper modification. The author however finds in the behaviour of pure oxide of copper to phosphoric acid, according to which it possesses in his opinion a tendency to unite always in double atoms, a reason for doubling the above formula, and giving to the acid contained in it the rational formula $4PO^5+4HO$.

M. Fleitmann considers it proved that the production of the different metaphosphoric acids is owing to a polymerism of the radical, in accordance with which the different acids may be expressed by the following polymeric series:—

Monometaphosphoric acid.....	PO^5+HO
Dimetaphosphoric acid	$2PO^5+HO$
Trimetaphosphoric acid.....	$3PO^5+3HO$
Tetrametaphosphoric acid.....	$4PO^5+4HO$

Led by this idea, he has endeavoured to ascertain the rational formulæ for the other two metaphosphoric acids, of the deliquescent Graham's salt, and of the previously known insoluble soda salt. His experiments have as yet not led to any definite results. He hopes however to succeed in ascertaining the two wanting formulæ.—*Berlin Berichte.*

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of Sugar and Starch by means of Sulphate of Copper. *By* H. Fehling.

About two years since, being engaged in some researches on diabetic urine, I was led to make several experiments on the estimation of diabetic sugar. As I had no suitable polarizing apparatus at my

disposal, I tried Barreswill's plan with an alkaline solution of sulphate of copper, and found the test to succeed perfectly when the solution of copper was of such a composition that it is not decomposed on ebullition alone. I at that time published the method pursued by me in my investigations on diabetic urine, and mentioned that I had likewise employed the method for technical purposes, as for instance determining the amount of sugar in beet-root, as also the starch in potatoes and corn. I have since repeatedly employed this test for the same purposes, and also for the estimation of sugar in grape-juice, and am convinced that the method is peculiarly well suited for technical purposes, as it quickly leads to a result which is at least as near the truth as is requisite for these purposes. In the case of urine, I have ascertained, by dissolving a certain amount of pure diabetic sugar in normal urine, that the constituents of the normal urine do not prevent the estimation of the amount of sugar.

In like manner I have mixed a solution of grape-sugar with pectine, tannin and mucilage in small quantities, and have ascertained that they do not affect the determinations. To check the results, I also determined the sugar in the juice of the grape by fermentation. With from 18 to 22 per cent. of sugar, I found in this manner from 0·4 to 0·8 per cent. less than by the copper test; this may be owing partly to the latter method giving too high an amount, and partly to the fact that a small portion of the sugar easily escapes fermentation when the solution is not sufficiently diluted. Grape-juice, diluted, precipitated with basic acetate of lead and filtered, gave the same amount of sugar as before precipitation; with some apple-juice, a little more sugar was found by the copper-test than when it had been previously precipitated with basic acetate of lead.

Copper Solution.—As is well known, the solution contains sulphate of copper, neutral tartrate of potash and caustic potash; it is absolutely essential that these constituents should be present in the correct proportions; when this is not the case, it rapidly decomposes by exposure to the light without any addition of sugar, instantly in the direct light of the sun, and also on heating and boiling; protoxide of copper separates, or a green basic salt, and with heat also brown oxide. Such a solution changes rapidly, and gives dissimilar results. The following solution of copper has kept unaltered for two years; it may be boiled for some length of time without in the least being decomposed.

40 grms. pure crystallized sulphate of copper are dissolved in about 160 grms. of water; on the other hand, a solution of 160 grms. neutral tartrate of potash are dissolved in little water with 600 to 700 grms. of a solution of caustic soda* of 1·12 spec. grav., and the solution of sulphate of copper gradually added to this basic solution, when the whole is diluted to form 1154·4 cub. centim.† at 59° F.

* I generally employ in most investigations caustic soda, as it is more easily obtained pure than caustic potash.

† I formerly took a litre as the volume, which I have altered to the present in order to render the calculation easier.

Solution of Sugar.—In order to determine the amount of copper salt reduced by a certain quantity of sugar, I first took cane-sugar, which was converted, by boiling with tartaric acid or sulphuric acid, into grape-sugar. I soon however became convinced that the results were not always accordant, from the last portions of the cane-sugar being very slowly metamorphosed. I therefore preferred, in the estimation of the amount of copper, using pure grape-sugar, and employing sugar prepared from honey, and also from urine which had been completely dried at 212°, and furnished on analysis the composition $C^{12} H^{12} O^{12}$. I now determined the weight of protoxide of copper, which was obtained from a certain quantity of the grape-sugar with a slight excess of the copper solution; the amount of the protoxide was determined by ignition with nitric acid, or with some peroxide of mercury, as oxide of copper. With 180 parts by weight of grape-sugar I obtained, in numerous experiments, always between 375 and 395 parts by weight of oxide of copper, that is, for 1 equiv. of $C^{12} H^{12} O^{12}$ (180) 10 equivs. oxide ($10 \times 39{\cdot}75$). The reason why the result found is lower than the calculated one is, that a small portion of the protoxide of copper always becomes oxidized by exposure to the air in the washing, and dissolves.

I then determined the proportion of the copper salt to the grape-sugar, by adding to a definite volume of the copper solution a normal solution of sugar until the whole of the copper salt had completely separated. In these experiments I likewise consumed, for 1 equiv. grape-sugar (180), 10 equivs. sulphate of copper (1247·5). 1 litre of the copper solution, prepared as above directed, contains 34·650 grms. sulphate of copper, and requires consequently for reduction 5 grms. of dry grape-sugar ($C^{12} H^{12} O^{12}$) for $34{\cdot}650 : 5 = 1247{\cdot}5 : 180$, or $= 6{\cdot}930 : 1$.

10 cub. centim. of the copper solution represent therefore 0·050 grm. of dry grape-sugar.

Method.—In examining a saccharine liquid, I dilute a certain weight 10 or 20 times the volume in cubic centimetres, so that it contains 1 per cent. of sugar at the very most; with the juice of the grape, for instance, I take 10 grms., and add so much water that the volume of the liquid amounts to 200 cub. centim.

On the other hand, 10 cub. centim. of the copper solution are diluted with 40 cub. centim. of water, the liquid heated to boiling, and the solution of sugar added to it until the whole of the copper is exactly reduced. The closer this point is attained, when all the copper salt is separated, the redder and more copious is the precipitate and the more quickly does it subside; a sample of the liquid filtered should not show the presence of copper with sulphuretted hydrogen or with ferrocyanide of potassium*. If the filtered solution contains an excess of sugar, it soon exhibits a yellowish colour. As with some practice an experiment is made in a few minutes, a

* In testing with the yellow prussiate, the liquid should be rendered slightly acid with hydrochloric acid, as no precipitate is produced by it in the alkaline liquid though it contain copper.

second check experiment can easily be made, in order to ascertain precisely the point when the whole of the copper salt is reduced with the smallest amount of sugar. Since the copper salt is instantly reduced by the sugar, no long boiling is requisite if the copper solution is always kept boiling or nearly on the boil. The addition of sugar immediately reduces the corresponding amount of copper. On continued ebullition, no further reduction results without a fresh addition of sugar.

The volume of the solution of sugar consumed contains, according to what has been above stated, 0·050 grm. grape-sugar. Now since the amount of sugar in the liquid is inversely proportional to the volume consumed, we have, in order to ascertain the per-centage amount of sugar, to divide 5 by the consumed quantity of sugar solution in cubic centimetres, if the solution of sugar was not diluted; but if it was diluted, for instance 20 times, we have to divide $20 \times 5 = 100$ by the number of cubic centimetres used.

When with solutions containing a large amount of sugar, grape-juice for instance, 20 per cent., it is not desirable to dilute them, a proportionately greater amount of the solution of sulphate of copper must be taken in order to diminish the error of observation; I however prefer diluting the solution of sugar for several reasons. Of diabetic urine, grape-juice, &c., I dilute, as above stated, a certain weight in grammes 10 or 20 times its volume in cubic centimetres. $\frac{5.10}{n}$ or $\frac{5.20}{n}$, where n denotes the number of cubic centimetres of solution of sugar used for 10 cub. centim. of copper solution, is therefore the per-centage amount of grape-sugar, $C^{12}H^{12}O^{12}$, contained in the liquid examined. Other volumes may be used besides those above given, for instance 20 cub. centim. of copper solution corresponding to 0·100 grm. $C^{12}H^{12}O^{12}$, and I use this larger volume for grape-juices containing very much sugar. Instead of determining the liquids according to the volume, it may also be done according to weight in grains as well as in grammes. As many may like to have the calculations spared them, I will here give the suitable proportions by weight.

Prepare from 1 oz. sulphate of copper, 3 oz. cream of tartar, ½ oz. pure potash, and 14 to 16 oz. of solution of caustic soda (in 1·12 spec. grav.), and water 13852 grs. = 28 oz. 6 drms. and 52 grs. solution. 1000 grs. of the solution contain 34·65 grs. of sulphate of copper, and correspond therefore to 5 grs. of grape-sugar. In experimenting, the copper solution is diluted with 4 times the quantity of water, and it is also advantageous to dilute the sugar solution. The amount of the sugar is calculated according to the proportion above stated; 200 grs. of copper solution require 1 gr. of $C^{12}H^{12}O^{12}$ for reduction.

In order to determine cane-sugar by means of the copper liquid, it must be converted into grape-sugar by the action of sulphuric or tartaric acid. In this operation it is requisite to apply heat for several hours, to be certain that the whole of the grape-sugar is

metamorphosed. The same applies to starch. There is no other test, it is true, in this case, than to take a sample from time to time until the quantities consumed remain the same.

In these experiments we obtain the quantity of grape-sugar proportional to that of the cane-sugar or of the starch; from which however their amount may be easily calculated, since 100 parts by weight of grape-sugar, $C^{12} H^{12} O^{12} = 95$ parts by weight of cane-sugar, $C^{12} H^{11} O^{11}$, or 90 parts of anhydrous starch, $C^{12} H^{10} O^{10}$.

It is probable that the foreign substances which are contained in the urine and vegetable juices likewise precipitate or reduce some copper. The amount may frequently prove to be somewhat too high according to this method, especially in several vegetable juices. Many foreign ingredients can be precipitated by the addition of a little basic acetate of lead. This easy and quick process is consequently well adapted for technical purposes, where the chief object is to obtain a quick result in an easy manner rather than absolute accuracy.

The above had been written some time when I received M. Schwartz's paper on the estimation of starch in the moist way. That chemist employs a solution of copper similar to the one above described. His results however differ insofar, that according to him only 3 grms. of sulphate of copper are reduced by 1 grm. of starch converted into sugar, or 162 starch, corresponding to 486 sulphate of copper, *i. e.* $\frac{486}{124{\cdot}75} = 3{\cdot}9$, or nearly 4 equivs. of the latter. 1 part by weight of starch sugar would consequently only reduce 2·7 parts by weight of sulphate of copper, whilst in my experiments the above quantity of sugar always reduced 6·9 parts of sulphate of copper. These differences rendered a repetition of M. Schwartz's experiments necessary. The solution of copper prepared according to his direction, which has the advantage of containing less caustic soda and tartrate of potash than the one I have described, is instantly decomposed by sunlight; after a short time in daylight; and very quickly when heated upon the water-bath, with separation of protoxide of copper. I imagined that the best way to test it would be to mix it with a lesser quantity of pure grape-sugar than requisite for perfect decomposition, and to determine the amount of protoxide of copper formed. In several such experiments with 0·180 pure diabetic sugar, 0·420–0·0470 grm. oxide of copper was obtained, whilst with the solution I have described 0·397 was obtained; but according to Schwartz only 0·159 oxide should have been obtained. That more oxide of copper was obtained in the experiments made with pure grape-sugar than ought to have been the case is probably owing to the circumstance, that a portion of the protoxide of copper is reduced by the mere application of heat; that Schwartz reduced much less copper must probably be ascribed to the imperfect conversion of the starch into sugar; at all events it is my intention to make further experiments on this point as soon as possible.—Liebig's *Annalen*, October 1849.

On the Action of Sugar and Sulphuric Acid upon Organic Matters, in reference to Pettenkofer's *Test for Bile. By* Dr. M. S. Schultze.

This test, which, as is well known, is based upon the production of a reddish-violet colour when the substance is acted upon by sulphuric acid and a solution of sugar, was recommended by M. Will as an infallible means of detecting bile, and applied by him as a means of determining the nature of organs existing in those animals in which distinct biliary organs had not been recognized, by submitting their secretions to its action.

The author, however, on applying it in the manner recommended by M. Will, found that all the soft parts of minute Crustacea, Annelida, Entozoa, Planariæ, Polypes and Infusoria exhibited the reaction equally in the case of the supposed biliary organs and other soft parts of the body. M. Schultze was led by the discovery of this fact to the investigation of the general conditions under which this colour was produced.

On washing various parts of healthy higher animals for several hours with water, and subjecting them to this test, he found that the so-called proteine substances especially exhibited the reaction, *e. g.* the fibres of the muscles, whilst the gelatinous tissues gave a dirty yellowish-red colour, and the elastic fibres experienced no change. Moreover, on treating thin sections of plants in the same manner, he found that the vegetable matters corresponding to the proteine compounds of animals were strongly reddened, whilst the starch and cellulose were unaltered.

M. Will was aware that other organs besides those secreting or excreting bile were reddened by the test; but he considered this to arise from the mere infiltration of the organs with bile. M Pettenkofer recommended its use for the recognition of bile in liquids or semisolid substances, by preparing an extract from them by alcohol. He did not apply it to solid animal matters; and before subjecting albuminous solutions to its action, he recommended the separation of the albumen by coagulation. The reaction is however equally well shown with solutions of caseine and globuline. Ordinary cow's milk and aqueous or sulphuric solutions of pure caseine also exhibit the colour distinctly. Solutions of chondrine and gelatine exhibit no trace of the colour. Oleine exhibits it in great perfection; whilst stearine, margarine and cholesterine do not so.

M. Schultze succeeded in isolating the substance, which acquires the red colour as follows:—The white of egg was diluted with about 5 parts of water, filtered, sulphuric acid gradually added, the mixture being constantly shaken, until the precipitate at first formed is redissolved. The heat of the mixture was kept below 140° F. A few drops of a strong solution of sugar were then added to the solution, when the filtrate gradually acquired a violet-red colour, the rapidity of its formation depending upon the colour. If the syrup causes any turbidity, more acid is required. In about ten to fifteen

minutes ammonia is added to the solution as long as any precipitate is formed. Great excess of ammonia redissolves the precipitate, and must be avoided. The violet flaky precipitate is separated by filtration from the solution of sulphate of ammonia, and washed until the water contains no further trace of solid matter, and neither reddens litmus nor is precipitated by chloride of barium.

At the ordinary temperature it is dissolved by concentrated sulphuric acid with a purplish-red colour, by the dilute acid with a violet-red colour. Muriatic acid renders it violet, and nitric acid yellow. It is readily soluble in solution of potash and ammonia. It is precipitated from the ammoniacal solution by chloride of barium, neutral and basic acetate of lead; but not by lime-water, nitrate of silver nor sulphate of copper. These properties, which are neither those of any pure proteine substance nor of a compound of such with sulphuric acid, show clearly that the substance is peculiar. Its elementary analysis has not yet been made.

The elementary tissues examined in respect to this test by M. Schultze not previously mentioned may be arranged as follows:—Those exhibiting the characteristic reaction were found to be, animal substances, striated muscular fibre, the unstriated muscular fibre of the intestines and œsophagus, the contractile fibres of arteries, nerve-fibres, ganglion-globules, and other elements of the nervous system, the globules of the blood, of mucus and pus, the epithelia of serous and mucous membranes, cuticle, hair, feathers, the horns of the Ruminantia, and whalebone; of vegetable substances, legumine, vegetable albumen and gluten, and the cellular portions of Fungi and Algæ.

The following substances were either unaffected or rendered of a dirty brown, or some other colour differing from the peculiar reddish-violet:—Animal: the fibres of tendon, cellular tissue, serous membranes, the fibres of elastic tissue, the gelatine of bones, the basis of cartilage, chitine and silk. Vegetable: cellulose, gum, amylum and vegetable mucus. The substances, before being submitted to the test, should be thoroughly washed with water, to remove the albuminous constituents when present.—Liebig's *Annalen*, Sept. 1849.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Red Colouring Substance of Exotic and Indigenous Rhubarb, and its Application to the Arts and Pharmacy. *By* M. Garot.

The following are the results of the author's investigation:—

1. By treating 1 part of rhubarb with 4 parts of nitric acid, the residue which is not acted on by the acid consists of a peculiar sub-

stance, amounting in the indigenous rhubarbs to from 8 to 10 per cent., and in the exotic rhubarbs to from 15 to 20 per cent.

2. This substance, which the author calls *erythrose*, is yellow when derived from indigenous, and of an orange colour when procured from exotic rhubarbs. It is almost entirely soluble in alcohol and in æther, which on evaporation furnish *rhabarbaric* or *erythrosic acid.*

3. Erythrose forms with the alkalies red or purple compounds, susceptible of application to the arts and to pharmacy.

4. The erythrosate of potash possesses a tinctorial power (in alcohol or any other non-acid liquid) six times greater than cochineal, and the red obtained is brighter and as stable.

5. The erythrosate of ammonia, after dissipation of the excess of alkali, possesses the same properties as the potash compound, and its tinctorial power is at least four times greater. It may be employed as a red ink with as much advantage as that made with cochineal or carmine.

6. This erythrosate may be used with very great advantage in perfumery, for imparting a rose colour to soaps.

7. The erythrosate of potash or ammonia from the different rhubarbs should be arranged, as regards their tinctorial power, in the following order:—Russian rhubarb, Chinese rhubarb, indigenous rhubarb.

8. The tinctorial power of the erythrose from the exotic rhubarbs being at least three times stronger than that from the indigenous rhubarb, it will furnish a ready means of ascertaining their origin, especially if, making a comparative examination, account be at the same time taken of the amount of erythrose, which is from 15 to 20 per cent. and of an orange colour from the exotic rhubarbs, and from 8 to 10 per cent. and yellow from the indigenous.

The author adds in a postscript, that by slightly modifying the mordants usually employed, he has succeeded in fixing upon silk and wool some very beautiful tints, similar to those furnished by cochineal. In these experiments the indigenous rhubarb constantly furnished the most brilliant red, contrary to what would have been supposed from what has been stated relatively to the colouring of alcohol. The dyed specimens had been exposed to the light for nearly a month without having experienced the least change.

These results may lead to the cultivation of rhubarb as a dyeing material, becoming of considerable importance.—*Journ. de Pharm. et de Chim.*, Jan. 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some deoxidizing Effects of Carbon. *By* Prof. SCHÖNBEIN.

1. WHEN ordinary charcoal powder is agitated, even but for a few minutes, with an aqueous solution of perfectly pure perchloride of iron, the latter, when filtered, strikes a deep blue colour with ferridcyanide of potassium, showing that under the above circumstances protochloride of iron is formed. When a definite quantity of the solution of the perchloride is treated long enough, and with a sufficient quantity of charcoal powder, the whole of the perchloride is converted into protochloride. This change is effected the more quickly the finer the charcoal is powdered, on which account calcined lamp-black is far more effective than ordinary charcoal powder. It deserves to be mentioned that even pulverized coke produces a similar effect upon the salt of iron.

2. The sulphate, nitrate and acetate of the peroxide of iron, dissolved in water, are completely converted into protosalts by agitation with charcoal powder; whence we are led to conclude, that all persalts of iron, dissolved in water or in any other menstruum, may be converted by carbon, even without the assistance of heat, into protosalts.

With respect to the behaviour of carbon towards a solution of the pernitrate of iron, the following statements may be mentioned. If the solution is so dilute that it appears of a light yellowish-brown colour, and it is shaken for a few minutes with charcoal powder, the filtered liquid is of a much darker colour than the original solution. After further brief treatment with fresh charcoal, the colour of the solution becomes much darker; and after a third or fourth operation of the same kind, the liquid appears almost colourless, in which case it now contains no longer a trace of the persalt of iron, but only protosalt. This darkening of the colour arises from the charcoal removing not only oxygen from the solution of the persalt of iron, but some nitric acid at the same time; which gives rise to the formation of basic pernitrate of iron, the cause of the dark colour.

3. When the solution of the ferridcyanide of potassium is shaken only for a few minutes with ordinary charcoal powder, the filtered liquid strikes a pretty deep blue colour with perchloride of iron, or

the solution of any other persalt free from protoxide. The same solution, agitated for a sufficient time and with a sufficient quantity of charcoal powder, is so changed, that it furnishes a copious dark blue precipitate with a solution of a persalt of iron, or leaves on evaporation a yellowish residue, which I have not yet been able to examine more closely, but which appears to consist for the greater part of ferrocyanide of potassium.

Regarding the dissolved ferridcyanide of potassium as a double salt, consisting of prussiate of potash and prussiate of the peroxide of iron, and the dissolved ferrocyanide of potassium as prussiate of protoxide of iron and potash, the above effect of the carbon might be explained from a conversion of the per- into the protoxide of iron.

4. A solution of the perchloride of mercury, agitated sufficiently long with a suitable quantity of charcoal powder, is rendered tasteless and incapable of furnishing peroxide of mercury with solution of potash. The perchloride is converted under these circumstances into protochloride.

5. A dilute solution of pernitrate of mercury, perfectly free from protoxide, shaken but for a few minutes with charcoal powder, and then filtered, is rendered very turbid by muriatic acid or a solution of chloride of sodium arising from precipitated protochloride of mercury, which proves that the charcoal converts a portion of the pernitrate of mercury immediately into protosalt even in the cold. By shaking the same solution of pernitrate three or four times in quick succession with fresh portions of charcoal powder, I succeeded in obtaining, in the course of a quarter of an hour, a protosalt perfectly free from peroxide. This property of carbon may be usefully employed in freeing soluble protosalts of mercury from any admixture of persalt.—Poggendorff's *Annalen*, lxxviii. p. 521.

On the Composition of the Fæces of Man in Health and in Diabetes Mellitus. *By* John Percy, M.D., F.R.S.

Part of the following paper was read to the Chemical Section of the British Association at Cambridge, 1845, and subsequently published in Dr. Day's translation of Simon's 'Animal Chemistry.' But as that work is not generally in the hands of chemists, I now present the entire paper in the 'Chemical Gazette.'

The analyses were made with particular reference to the pathology of Diabetes mellitus. To some it might appear useless to expend time in ultimate analyses of the solid egesta of man; but there are considerations, physiological as well as pathological, which render it desirable that such analyses should be made.

The patients from whom the fæces were obtained were under my own care; two of them were in the Queen's Hospital when I was physician to that institution. Two of the cases have appeared in the 'Medical Gazette;' but the third, upon which I have a very great number of observations, has not yet been published. Analyses

of the fæces of man in health and under different conditions of diet, and of a patient affected with Icterus, will also be introduced.

Ultimate Analyses of the Fæces.

In these analyses chromate of lead was invariably used as the oxidizing body.

The desiccation of the fæces, preparatory to analysis, was effected at 212° F., or some degrees above. In the second analysis the matter employed was generally subjected to the desiccating process for a much longer time than in the first, so that the correctness of the amount of hydrogen might be satisfactorily tested.

1. *Of the Fæces in Health.*—The individual whose fæces were subjected to analysis was a young man, aged thirty, who had taken the ordinary diet of this country, and who appeared to be in the enjoyment of perfect health.

First Combustion.—7·41 grs. gave of HO 4·43 =H 6·64 per cent. Of CO^2 12·55 =C 46·18 per cent.

Second Combustion.—7·24 grs. gave of HO 4·44 =H 6·81 per cent. Of CO^2 12·28 =C 46·23 per cent.

Incineration.—50·13 grs. gave of ash 8·21 =16·37 per cent.

Nitrogen.—Not determined.

Mean of the Two Combustions.

Carbon	46·20
Hydrogen	6·72
Nitrogen, Oxygen*	30·71
Ash	16·37
	100·00

These results are very nearly the same as those obtained by Dr. Lyon Playfair at Giessen (Liebig's Anim. Chem., translated by Gregory, p. 285, 1842):—

Dr. Playfair's Analysis.

Carbon	45·24
Hydrogen	6·88
Nitrogen, Oxygen	34·73
Ashes	13·15
	100·00

These facts are worthy of attention, as they seem to show, that, under ordinary circumstances of health, the composition of the fæces is more uniform than we might *à priori* have inferred. The first analysis, it will be borne in mind, was of the fæces of a man in this country, and the second of the fæces of a soldier at Giessen.

* Sulphur is doubtless also present. When fæces are incinerated in a platinum crucible, the metal is somewhat attacked.

2. *Of the Fæces of a Man undergoing the curious and rigorous Discipline of "Training" for Prize-fighting.*—Age, 22; height, 5 ft. 6 in.; weight, 8½ st. This individual, it will scarcely be doubted, must have been in the most perfect state of health. I wish to direct particular attention to his diet. He breakfasted at 9 A.M., and ate 1 lb. of mutton, weighed before cooking. He dined at 1 P.M., and ate the same quantity of mutton with the addition of about 2 oz. of bread. And again, at supper, at 8 P.M., he had the same quantity of mutton. At each meal he drank half a pint of ale, but no other liquid at any other time of the day. Nor did he eat any other vegetable matter whatever besides the small quantity of bread mentioned. He walked seventeen miles daily.

First Combustion.—5·35 grs. gave of HO 3·43 =H 7·12 per cent. Of CO^2 9·73 =C 49·60 per cent.

Second Combustion.—5·74 grs. gave of HO 3·62 =H 7·01 per cent. Of CO^2 10·52 =C 49·98 per cent.

The difference between these two combustions in respect to the carbon is greater than should be tolerated, but is not of much consequence in the present investigation, in which precise formulæ are not concerned.

Incineration.—31·42 grs. gave of ash 4·56 =14·51 per cent.

Mean of the Two Combustions.

Carbon	49·79
Hydrogen	7·06
Nitrogen, Oxygen	28·64
Ash	14·51
	100·00

I should remark, that after passing a current of dry air, in the usual apparatus, over these fæces during a considerable time, there still remained in the tube connected with the reservoir of water some clear and colourless liquid, which had a strong, peculiar and offensive odour, and which powerfully reddened litmus. I continued to pass the air through the tube for a much longer time than usual, in order to remove the liquid, which at first I did not suspect to be more than water. Having since examined a specimen of pure butyric acid, I was immediately struck by the similarity of odour between it and the liquid mentioned above; and I am now disposed to believe that the liquid in question consisted of, or at least contained, butyric acid in large proportion. That acid has been discovered in the fæces by Dr. Ragsky of Vienna.

3. *Of the Fæces of a Boy,* Stubbs, *aged* 7 (*Diabetes*).—They were hard, and not of the natural consistence of health.

First Combustion.—5·44 grs. gave of HO 3·35 =H 6·83 per cent. Of CO^2 8·76 =C 43·94 per cent.

Second Combustion.—4·72 grs. gave of HO 3·01 =H 7·09 per cent. Of CO^2 7·58 =C 43·79 per cent.

Incineration.—30·76 grs. gave of ash 6·18 =20·09 per cent.

Mean of the Two Combustions.

Carbon	43·86
Hydrogen	6·96
Nitrogen } Oxygen }	29·09
Ash	20·09
	100·00

The proportion of saline matter in this analysis is very large, and probably depended upon constipation.

4. *Of the Fæces of a man,* Flint, *aged* 48 (*Diabetes*), *while restricted to an Animal Diet.*—They were of moderate consistence. This analysis was made by my former pupil, Mr. Stallard, in my laboratory.

First Combustion.—8·22 grs. gave of HO 5·61 =H 7·58 per cent.
Of CO^2 16·43 =C 54·51 per cent.

Second Combustion.—8·57 grs. gave of HO 5·84 =H 7·57 per cent.
Of CO^2 17·03 =C 54·20 per cent.

Nitrogen (determined by myself). Will's process was adopted. 6·29 grs. gave of metallic platinum 5·33 =N 12·01 per cent.

Incineration (*by* J. P.).—61·01 grs. gave of ash 5·71 =9·36 per cent.

(*By* Mr. Stallard).—9·35 grs. gave of ash 0·87 =9·34 per cent.
27·96 grs. gave of ash 2·57 =9·26 per cent.

Mean of the Two Combustions.

Carbon	54·35
Hydrogen	7·57
Nitrogen	12·01
Oxygen	16·71
Ash	9·36
	100·00

5. *Of the Fæces of* Flint, *while taking* 3 *oz. of Fat Bacon daily in addition to his usual Animal Diet.*—These fæces contained so large an amount of fatty matter, that it was impossible to reduce them to powder *per se.* When heated gently, they became soft, pasty, and almost of the consistence of semi-melted fat. A proximate analysis of them will be subsequently inserted.

First Combustion.—5·06 grs. gave of HO 4·22 =H 9·22 per cent.
Of CO^2 11·20 =C 60·36 per cent.

Second Combustion.—6·28 grs. gave of HO 5·25 =H 9·28.
Of CO^2 13·89 =60·32 per cent.

Incineration.—55·93 grs. gave of ash 7·40 =13·23 per cent.

Mean of the Two Combustions.

Carbon	60·34
Hydrogen	9·25
Nitrogen } Oxygen }	17·18
Ash	13·23
	100·00

6. *Of the Fæces of* Flint, *a few weeks afterwards, while restricted to Animal Diet of the Lean of Meat.*—As far as practicable all fat was removed.

First Combustion.—7·06 grs. gave of HO 5·05 =H 7·95 per cent.
Of CO^2 13·72 =C 53·00 per cent.

Second Combustion.—6·62 grs. gave of HO 4·77 =H 8·00 per cent.
Of CO^2 12·93 =C 53·27 per cent.

Incineration.—16·81 grs. gave of ash 2·96 =17·60 per cent.

Mean of the Two Combustions.

Carbon	53·09
Hydrogen	7·97
Nitrogen, Oxygen	21·34
Ash	17·60
	100·00

7. *Of the Fæces of a man,* Roberts, *aged* 37 (*Diabetes*).—With the exception of a small quantity of bread, his diet was exclusively animal.

First Combustion.—4·53 grs. gave of HO 3·07 =H 7·53 per cent.
Of CO^2 7·64 =C 45·99 per cent.

Second Combustion.—5·33 grs. gave of HO 3·67 =H 7·65 per cent.
Of CO^2 8·92 =C 45·64 per cent.

Incineration.—30·84 grs. gave of ash 10·77=21·18 per cent.

Mean of the Two Combustions.

Carbon	45·81
Hydrogen	7·59
Nitrogen, Oxygen	25·42
Ash	21·18
	100·00

8. *Of the Fæces of* Roberts, *while subsisting on a mixed Diet.*—At this time also he was greatly emaciated, in consequence probably of having been obliged to work, and not having been able to procure a due proportion of animal food.

First Combustion.—5·13 grs. gave of HO 3·36 =H 7·28 per cent.
Of CO^2 8·63 =C 45·88 per cent.

Second Combustion.—4·86 grs. gave of HO 3·18 =H 7·27 per cent.
Of CO^2 8·21 =C 46·07 per cent.

Incineration.—32·31 grs. gave of ash 7·14 =22·10 per cent.

Mean of the Two Combustions.

Carbon	45·97
Hydrogen	7·27
Nitrogen, Oxygen	24·66
Ash	22·10
	100·00

9. *Of the Fæces of a young Woman affected with Icterus in a mild form, and probably depending on functional derangement of the liver.*—They were brown, and not clay-coloured, as in severe jaundice.

First Combustion.—5·59 grs. gave of HO 3·66 =H 7·27 per cent.
Of CO^2 10·54 =C 51·42 per cent.

Second Combustion.—5·12 grs. gave of HO 3·37 =H 7·31 per cent.
Of CO^2 9·69 =C 51·61 per cent.

Incineration.—28·18 grs. gave of ash 3·41 =12·10 per cent.

Mean of the Two Combustions.

Carbon	51·51
Hydrogen	7·29
Nitrogen, Oxygen	29·10
Ash	12·10
	100·00

The following tables will show at a glance the relation in composition of the various specimens of fæces of which the analytical details have been recorded above.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbon	46·20	49·79	43·86	54·35	60·34	53·09	45·81	45·97	51·51
Hydrogen	6·72	7·06	6·96	7·57	9·25	7·97	7·59	7·27	7·29
Nitrogen, Oxygen	30·71	28·64	29·09	28·72	17·18	21·34	25·42	24·66	29·10
Ash	16·37	14·51	20·09	9·36	13·23	17·60	21·18	22·10	12·10
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The succeeding table will exhibit clearly the precise relation in composition of these fæces, the per-centage of each being calculated exclusive of ash.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbon	55·24	58·24	54·88	59·96	69·54	64·43	58·11	59·01	58·60
Hydrogen	8·03	8·25	8·71	8·35	10·66	9·67	9·62	9·33	8·29
Nitrogen, Oxygen	36·73	33·51	36·41	31·69	19·80	25·90	32·27	31·66	33·11
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

[To be continued.]

On the Chloride of Cyanogen and Titanium. *By* Prof. Wöhler.

In the author's former paper on titanium, it was mentioned that the chloride of titanium formed a definite compound with the chloride of cyanogen *. Without its existence, it is probable that the cubic crystals of titanium would have been still long regarded as pure titanium. It was this compound which, by its volatility and crystallizability, betrayed the presence of cyanogen in them. It became therefore a matter of interest to ascertain its quantitative composition.

* Chem. Gaz., vol. vii. p. 484.

This compound is instantly formed, with strong evolution of heat, when gaseous chloride of cyanogen is passed into chloride of titanium. In a very short time the latter is converted into a loose yellow crystalline mass.

The chloride of cyanogen and titanium is of a lemon-yellow colour and highly volatile. It begins to volatilize far below 212° F., and sublimes in transparent lemon-yellow crystals, which appear to be rhombic octohedra. It fumes very strongly in a moist atmosphere, and turns milk white, diffusing the pungent odour of the chloride of cyanogen. Water dissolves it to a perfectly clear solution, with disengagement of intense heat and evolution of gaseous chloride of cyanogen. It dissolves in warm chloride of titanium, and again separates in crystals on cooling. It absorbs ammoniacal gas with considerable disengagement of heat, and forms with it a deep orange-red compound, which also turns white in a moist atmosphere, and is dissolved by water with a partial separation of titanic acid.

The chloride of cyanogen and titanium is represented by the formula $CyCl+2TiCl^2$, according to which it should contain 75·56 per cent. of chloride of titanium.

3·008 grms. were employed for analysis; they were dissolved in water, and precipitated while boiling by ammonia. 0·964 grm. of calcined titanic acid was obtained, corresponding to 2·283 grms. or 75·89 per cent. of chloride of titanium.—*Göttingen Nachrichten*, Jan. 1850.

Chemical Examination of the Oil of Asafœtida.
By Dr. H. Hlasiwetz.

When asafœtida is treated with strong alcohol, the resin and oil it contains are dissolved, leaving a residue of gum. When the alcoholic extract is distilled, it leaves a concentrated solution of resin, which on being poured into water deposits the resin of a yellowish-white colour and almost free from smell. The oil can also be partly obtained by mixture with water; but a far larger amount is obtained when the resin, broken into small pieces, is distilled with water. The distillation is best conducted in a glass retort, which is connected with a Liebig's refrigerator.

This crude oil of asafœtida is a variable mixture of a higher and a lower sulphuret of the same radical. About half an ounce of oil is obtained from 1 lb. of the best asafœtida. It dissolves very readily in strong alcohol and æther, and also somewhat in water; it has at first a mild, but subsequently a pungent taste, does not redden the skin like other sulphuretted oils, and is neutral. When kept, it disengages a large amount of sulphuretted hydrogen, a property which it also imparts to the crude asafœtida. It cannot even be brought to a partial solidification by immersion in a freezing mixture. Its boiling-point is situated above 275°–284° F.; it is decomposed, with disengagement of sulphuretted hydrogen, by boiling.

In the fresh state it contains no oxygen, but only carbon, hydro-

gen and sulphur. When kept for some length of time exposed to the air, it becomes slightly acid, and its odour is somewhat different.

The following analyses of various samples and differently treated oils gave different results, leading to the formulæ—

I.	II.	III.	IV.
$\left\{\begin{matrix}C^{12}H^{11}S^{2}\\C^{12}H^{11}S\end{matrix}\right.$	$\left\{\begin{matrix}3(C^{12}H^{11}S^{2})\\C^{12}H^{11}S\end{matrix}\right.$	$\left\{\begin{matrix}5(C^{12}H^{11}S^{2})\\2(C^{12}H^{11}S)\end{matrix}\right.$	$\left\{\begin{matrix}C^{12}H^{11}S^{2}\\2(C^{12}H^{11}S),\end{matrix}\right.$

which express different sulphurets of the radical $C^{12}H^{11}$. The analyses furnished—

	I. Rectified oil distilled in a copper still: immediately after preparation.	II. Oil distilled in a copper still: after exposure for some time.	III. Oil distilled from a glass retort: immediately after preparation.	IV. Oil distilled from a glass retort between 248°–266° without boiling the liquid.
Carbon ..	67·13	64·24	65·46	69·27
Hydrogen	10·48	9·55	9·09	10·42
Sulphur ..	22·37	25·37	25·43	20·17
	99·98	100·16	99·98	99·86

In the distillation of the oil from metallic vessels, the metal is found to be acted upon by the sulphur; hence its influence upon the nature of the oil.

When the oil is distilled in a current of ammoniacal gas, it forms crystallized sulphuret of ammonium, with disengagement of sulphuretted hydrogen and the simultaneous appearance of an oil. The same is also formed when ammonia is passed into the oil.

Pentasulphuret of potassium, heated with the oil to 365° F., disengages a large amount of sulphuretted hydrogen, the oil being decomposed. The same occurs with the monosulphuret of potassium, already at 302°.

Muriatic acid gas changes the colour of the oil, first into red, then into violet, until it finally becomes black. The smell of the oil becomes pungent and resembling garlic, and the oil at last thick and smeary. Chlorine produces the same change of colour, muriatic acid and chloride of sulphur being formed, until finally a thick black tar remains, with a most insupportable odour of garlic and chloride of sulphur.

Caustic lime disengages no ammonia from the oil on calcination; it does not therefore contain any nitrogen. The salts of the metals which are precipitated from their acid solutions by sulphuretted hydrogen give precipitates of sulphurets when their solutions are mixed with the oil; salts of platinum and of mercury enter into definite combinations with it.

Potassium immediately produces a violent disengagement of gas, with formation of sulphuret of potassium; but the oil cannot be entirely deprived of sulphur in this manner. In one experiment the oil was found to contain 17·5, in another 9·4 per cent. of sulphur,

although it had been repeatedly treated with fresh quantities of potassium. The oil obtained however had an entirely different, aromatic odour. When the sulphuret of potassium formed is dissolved in a little water, and this solution decomposed with a somewhat diluted acetic acid, a remarkable odour of cinnamon is perceived as soon as the disengagement of sulphuretted hydrogen has ceased.

Oxide of silver forms sulphuret of silver with the oil; but the residual oil contains just as much sulphur after the treatment as before. The oxide of silver must therefore have completely oxidized and decomposed a portion of the oil.

Combinations of the Oil with Platinum.—The crude asafœtida oil gives with chloride of platinum precipitates which differ in composition according to the circumstances. The author has examined three such compounds, which however were not crystalline; only once a few glittering crystalline scales were obtained.

First Precipitate, obtained by mixing an alcoholic solution of the crude oil with solution of chloride of platinum, waiting until the whole of the precipitate had separated, which occupied a day and a half. It formed a rusty brown, very soft powder, void of smell, which did not dissolve in water, alcohol and dilute acids, and was decomposed by heat, the organic portion of the compound being volatilized with disengagement of a pungent odour. The powder first became darker, and finally quite black, and after the sulphur had been consumed burnt like tinder to perfectly pure platinum. Analysis gave—

Carbon	18·83	18·62	48 =	288·0	19·20
Hydrogen.....	3·19	3·15	44	44·0	2·90
Sulphur.....	17·53	..	16	256·0	17·04
Platinum	47·48	47·92	7	699·9	46·66
Chlorine	13·54	..	6	213·0	14·20
	100·00			1500·9	100·00

Second and Third Precipitate.—When a solution of the oil in weak spirit is heated to boiling with an excess of an alcoholic solution of chloride of platinum and filtered, a dark red precipitate is left on the filter, and after a short time a light yellow flocculent precipitate separates. They are both amorphous; the excess of oil and platinum may be washed out with alcohol, so that after the drying it is perfectly free from smell, and forms a fine powder. The first precipitate is reddish-brown, the latter pale yellow. When dry, both are insoluble; when heated, they behave like the precipitate I. The darker compound furnished on analysis—

Carbon.....	17·31	17·72	48 =	288	17·32
Hydrogen	3·03	2·97	44	44	2·64
Sulphur	18·87	..	19	304	18·29
Platinum	52·11	52·09	9	887	53·34
Chlorine	8·68	..	4	140	8·41
	100·00			1663	100·00

The light precipitate (3) gave the following numbers:—

Carbon	24·90	..	48 =	288·0	24·94
Hydrogen.....	3·87	..	44	44·0	3·80
Sulphur.....	20·26	..	15	240·0	20·76
Platinum	44·17	44·08	5	512·8	44·39
Chlorine	6·80	..	2	70·0	6·11
	100·00			1155·8	100·00

If we glance at the formulæ deducible from these results, it is evident that not one of the precipitates is a pure compound; all contain an admixture of sulphuret of platinum; but the organic substances, which may be expressed by the following formulæ for the precipitates 1, 2, 3, exhibit throughout a certain agreement. These formulæ are—

1. $5[C^{12}H^{11}S^2+PtS^2]+3[C^{12}H^{11}Cl^2+PtCl^2]$
2. $6[C^{12}H^{11}S^2+PtS^2]+2[C^{12}H^{11}Cl^2+PtCl^2]$
3. $7[C^{12}H^{11}S^2+PtS^2]+1[C^{12}H^{11}Cl^2+PtCl^2]$

The reasons which led the author to assume the group $C^{12}H^{11}S^2$ will now be further explained; and for this purpose, we shall, in the first place, give the crude formulæ, and their calculated results, from the analyses of crude oil of different preparations, compared with the mean found from several well-accordant analyses. 1 is the oil distilled from a copper still immediately after preparation; 2, distilled oil, of a different preparation, from a copper still, after exposure for some time; 3, oil distilled from a glass retort; 4, oil distilled from a glass retort, but below the boiling-point:—

1.	C .. 67·15	24	= 144	67·4	2.	C .. 64·28	48	= 288	64·8
	H .. 10·48	22	22	10·2		H .. 9·55	44	44	10·0
	S .. 22·37	3	48	22·4		S .. 25·37	7	112	25·2
	100·00		214	100·0		100·00		444	100·0
3.	C .. 65·48	84	= 504	65·2	4.	C .. 69·27	36	= 216	69·1
	H .. 9·09	77	77	10·0		H .. 10·46	33	33	10·5
	S .. 25·43	12	192	24·8		S .. 20·17	4	64	20·4
	100·00		773	100·0		100·00		313	100·0

Derived Oils of the Formula $C^{48}H^{45}S^3$.—The following are the compositions of modified oils, which were obtained,—I. by shaking the crude oil with a concentrated solution of oxide of lead in potash until no more sulphuret of lead was formed, or II. by digesting the crude oil for fourteen days with hydrated oxide of lead. These two oils gave on analysis the following results:—

	I.	II.			
Carbon.....	60·16	60·76	48 =	288	60·52
Hydrogen	6·43	9·52	44	44	9·24
Sulphur	29·85	29·72	9	144	30·24
	99·44	100·00		476	100·00

The oil I. has an agreeable odour of rosemary and lavender; II. is less aromatic, and smells more like the crude oil.

An oil is also obtained, which agrees with oil I., when sulphurous acid is passed into the crude oil to which a little water has been added; the oil becomes milky, and after standing deposits a resinous substance. When the oil is washed with a solution of carbonate of soda, and afterwards with water and rectified, an oil of the following composition is obtained after being deprived of water:—

Carbon	60·63	60·35	48	60·52
Hydrogen	9·48	9·24	44	9·24
Sulphur	31·02	..	9	30·24

An oil of the same composition and the aromatic odour of I. was also obtained on dropping the oil, in small portions at a time, upon soda-lime heated to 392° F. In this operation sulphuretted hydrogen is disengaged.

There was also obtained another oil of the same composition, but of a disagreeable odour, by keeping soda-lime and crude oil in a strong curved glass tube, sealed at both ends, for two days, at a temperature of 266° F. After this time the oil was distilled from the large arm into the smaller one, which was kept cold by ice, and analysed. The analyses of these two last oils agree with the preceding ones. In both cases the soda-lime contained acids belonging to the series $(C^2 H^2)^n O^4$

When this residue is exhausted with boiling water, and decomposed with dilute sulphuric acid, the liquid furnishes an acid distillate, from which, on saturation with carbonate of soda and decomposition with nitrate of silver, a mixture of different silver salts was obtained. A part formed a crystalline pellicle at the surface, and a part separated as a crystalline precipitate. These masses were separated by recrystallization into the following silver salts:—

1. *Metacetonate of Silver* was obtained as a granular salt. It gave on analysis—

	Found.	Calculated.
Oxide of silver	63·67	64·09
Atomic weight	182	181

2. *Valerianate of Silver* was obtained in the form of a pellicle, which soon became black by exposure to the light; it fused when heated, and gave—

	Found.		Calculated.
Oxide of silver	55·6	55·2	55·5
Atomic weight	209	210	209

Both acids likewise occur in the distilled water which passes over in the preparation of the oil from the crude asafœtida; this water is milky, smells strongly of the oil, of which it contains a pretty large quantity in solution, and has a slight acid reaction. Salts of baryta and silver do not furnish precipitates with it directly; but if it is neutralized with potash, evaporated to dryness, the brown mass dissolved in water, when a resinous mass separates, and the liquid is decomposed with sulphuric acid, a turbid product is obtained on

distillation, which treated as above furnishes two silver salts, one crystallizing in pellicles and scales, the other in tolerably hard granules. The first soon turned black by exposure to the light, and gave on analysis—

Carbon	28·05	..	10 =	60	28·70
Hydrogen	4·08	..	9	9	4·36
Oxygen	12·91	..	3	24	11·44
Oxide of silver	54·96	55·00	1	116	55·50
	100·00			209	100·00

The granular crystalline salt of the metacetonic acid gave—

Carbon	..	6 =	36	20·05
Hydrogen.....	2·59	5	5	2·74
Oxygen.....	..	3	24	13·24
Oxide of silver.....	63·57	1	116	63·97
			181	100·00

Products of Oxidation of the crude Oil of Asafœtida.—Nitric and chromic acids furnish with the crude oil acids belonging to the same series as the above.

Nitric Acid may act so violently that the oil takes fire. At first the fuming concentrated acid is added in very small portions to the oil, subsequently in larger quantities, and the whole boiled. The acid liquid produced is now diluted with much water and distilled; the product, which has an odour of musk, is saturated with carbonate of soda, concentrated, and decomposed with nitrate of silver. By frequent crystallization, two salts of silver are obtained,—1st, acetate, and 2nd, metacetonate of silver. The first gave on analysis—

Carbon.....	14·15	4 =	24	14·25
Hydrogen.....	2·01	3	3	1·80
Oxygen.....	14·96	3	24	14·49
Oxide of silver.....	68·88	1	116	69·46
	100·00		167	100·00

The metacetonate of silver was difficult to separate from the preceding salt, and was obtained in beautiful dendritic crystalline flakes. One determination of the atomic weight gave 174, and on analysis it furnished—

Carbon.....	16·90	..	5 =	30	17·39
Hydrogen	2·17	..	4	4	2·28
Oxygen	14·18	..	3	24	13·75
Oxide of silver	66·75	66·57	1	116	66·58
	100·00			174	100·00

Both salts burnt without fusing, and left a skeleton of silver of the form of the crystals. In the residual acid water, from which the two above acids had been distilled, oxalic acid was found.

Chromic Acid also oxidizes the oil, which is let fall in drops through a drawn-out tube into a paste of chromic acid and water. At first a liquid having the smell of acetic acid passes over, then

some undecomposed oil, and subsequently sulphurous acid. Finally, an odour of sulphuretted hydrogen is given off. If the distillation is now carried on further with a fresh receiver, metacetonic acid passes over: the silver salt which was obtained furnished 66·3 oxide of silver.

We find consequently among the products of oxidation of asafœtida oil the whole series of acids from the oxalic to the valerianic, with the exception of the butyric acid, which originate, according to the author, from the hydrocarbon $C^{12}H^{11}$.

Mercurial Compounds of the Oil of Asafœtida.—Perchloride of mercury instantly produces, in alcoholic solutions of the oil of asafœtida, a copious white precipitate, which soon turns gray by the deposition of sulphuret of mercury. Hot solutions of the two substances give a precipitate more quickly, but it is not so white. The liquid immediately acquires an offensive odour of garlic and a very acid reaction. Muriatic acid is formed in this operation; and this produces the same smeary, brown, tar-like substance which was described when speaking of the behaviour of this acid or of chlorine upon the oil.

The precipitate produced by the perchloride of mercury may be separated into two compounds by treatment with boiling alcohol. The one, which is present but in small quantity, dissolves in the alcohol, the other forms the residue. The substance dissolved by the alcohol separates from it in microscopic crystals; and after being once dried, is very difficult to dissolve in alcohol, is perfectly insoluble in water, and but very sparingly soluble in nitric acid. One drop of muriatic acid added to the nitric acid, instantly causes the salt to disappear. It contains mercury and chlorine in the same proportion as the perchloride of mercury; when treated with solution of potash, it turns yellow. When heated, it turns brown, diffuses a pungent odour of garlic, and subsequently turns black. The sulphur burns away with a blue flame, and finally the whole entirely disappears. Analysis gave—

Carbon	14·03	14·10	..	24	=144·0	14·65
Hydrogen	2·39	2·54	..	20	20·0	2·13
Chlorine	10·93	..	..	3	106·5	10·83
Mercury	61·19	62·34	61·08	6	600·0	61·05
Sulphur	11·46	..	..	7	112·0	11·39
	100·00				982·5	100·00

Whence the author deduces the formula—

$$[C^{12}H^{10}S^2 + 5HgS] + [C^{12}H^{10}Cl^2 + HgCl]$$
$$= 2[C^6H^5S + 2\tfrac{1}{2}HgS] + [C^6H^5Cl + \tfrac{1}{2}HgCl]$$

The other compound insoluble in alcohol forms when dry a very delicate grayish-white powder, without odour or taste. Nitric acid leaves on boiling a white crystalline substance, which instantly dissolves on the addition of some muriatic acid. When heated, it behaves precisely like the preceding compound. Mixed with solution of potash, it instantly turns black; whence it follows that it contains protochloride of mercury. The analyses gave—

Carbon	1·72	1·77	2·22	12=	72	2·52
Hydrogen	0·43	..	0·67	10	10	0·39
Chlorine	10·68	10·65	10·88	8	284	9·95
Mercury	76·49	75·60	76·40	22	2200	77·05
Sulphur	10·04	..	..	18	288	10·09
	100·00				2854	100·00

Corresponding to the following formula—

$$[C^{12}\,H^{10}\,S^{8}+2HgS]+4(Hg^{2}\,Cl)+4(Hg^{3}\,S^{2}\,Cl)$$
$$=[C^{6}\;H^{5}\;S^{4}+\;HgS]+2(Hg^{2}\,Cl)+2(Hg^{3}\,S^{2}\,Cl).$$

The author supposes the radical $C^{6}\,H^{5}$ in these two compounds, produced by the splitting of $C^{12}\,H^{10}+H$. This radical is contained, according to the author, in the soluble salt as a simple chloride and sulphuret combined with the analogous compounds of sulphur and chlorine with mercury; but in the insoluble salt it is contained as quadrisulphuret of allyle with sulphuret of mercury. It also contains the entire amount of the insoluble mercurial compounds produced at the same time in the form of calomel, together with the compound of sulphur and chlorine with mercury ($=Hg^{3}\,S^{2}\,Cl$).

With respect to this reaction, it has already been observed that the presence of free muriatic acid is apparent, from which we may conclude that a reduction of the perchloride of mercury occurs.

The deportment of the mercurial compounds of the oil of asafœtida towards cyanide of potassium differs from that of the platinum compounds, and is highly remarkable; they furnish with cyanide of potassium oil of mustard. The oil alone furnishes no oil of mustard when treated with cyanide of potassium.

Oil of Mustard from Oil of Asafœtida.—The mercurial compounds of the asafœtida oil behave like the compound prepared from garlic oil by Wertheim. The small quantity of the oil of mustard which the author obtained was treated with ammonia, and concentrated by evaporation. In the small quantity of yellow ley left, some scattered groups of the long prismatic crystals, characteristic of the compound of oil of mustard and ammonia, soon became perceptible. That the whole did not congeal to a paste of crystals, was probably owing to a few drops of unaltered allyle being still mixed with the oil of mustard. The whole dissolved in water readily. Recently precipitated chloride of silver was very quickly dissolved by the solution, and perchloride of iron gave with the same solution a decided reaction of sulphocyanogen.

At the end of his memoir the author has appended the following grouping of the formulæ:—

Crude oils.	Products of oxidation.
$C^{24}\,H^{22}\,S^{3}$ { $C^{12}\,H^{11}\,S^{2}$ / $C^{12}\,H^{11}\,S$	$C^{10}\,H^{9}\,O^{3}=\overline{Va}$
$C^{48}\,H^{44}\,S^{7}$ { $3(C^{12}\,H^{11}\,S^{2})$ / $C^{12}\,H^{11}\,S$	$C^{6}\;H^{5}\,O^{3}=\overline{Met}$
$C^{84}\,H^{77}\,S^{12}$ { $5(C^{12}\,H^{11}\,S^{2})$ / $2(C^{12}\,H^{11}\,S)$	$C^{5}\;H^{4}\,O^{3}=\overline{Met\;A}$
$C^{60}\,H^{33}\,S^{4}$ { $C^{12}\,H^{11}\,S^{2}$ / $2(C^{12}\,H^{11}\,S)$.	$C^{4}\;H^{3}\,O^{3}=\overline{A}$
	$C^{2}\;H\;\;O^{3}=\overline{Fo}$
	$C^{2}\;\;\;O^{3}=\overline{O}$

New combinations produced.

$$C^{48}\,H^{44}\,S^{9}\,\{3(C^{16}\,H^{15}\,S^{3}) \qquad C^{36}\,H^{33}\,S^{2}\left\{\begin{matrix}C^{12}\,H^{11}\\C^{12}\,H^{11}\\C^{12}\,H^{11}\end{matrix}\right\}\,S^{2}$$

Platinum compounds.

$$5[C^{12}\,H^{11}\,S^{2}+Pt\,S^{2}]+3[C^{12}\,H^{11}\,Cl^{2}+Pt\,Cl^{2}]$$
$$6[C^{12}\,H^{11}\,S^{2}+Pt\,S^{2}]+2[C^{12}\,H^{11}\,Cl^{2}+Pt\,Cl^{2}]$$
$$7[C^{12}\,H^{11}\,S^{2}+Pt\,S^{2}]+\ [C^{12}\,H^{11}\,Cl^{2}+Pt\,Cl^{2}],$$

Mercurial compounds.

$$[C^{12}\,H^{10}\,S^{2}+\ 5Hg\,S]+[C^{12}\,H^{10}\,Cl^{2}+\ Hg\ \ Cl]=$$
$$2[C^{6}\ \ H^{5}\ \ S\ +2\tfrac{1}{2}Hg\,S]+[C^{6}\ \ H^{5}\ \ Cl\ +\tfrac{1}{2}Hg\ \ Cl]$$
$$[C^{12}\,H^{10}\,S^{8}+\ 2Hg\,S]+[\ 4(Hg^{2}\,Cl)+4(Hg^{3}\,S^{2}\,Cl)]=$$
$$[C^{6}\ \ H^{5}\ \ S^{4}+\ \ Hg\,S]+[\ 2(Hg^{2}\,Cl)+2(Hg^{3}\,S^{2}\,Cl)].$$

The author makes the following observations with regard to the *resin* and *gum* from asafœtida.

The *resin*, as procured by the treatment described at the beginning of this paper, is dirty white, but soon turns rose-red in the air; it is probably owing to it that the crude asafœtida acquires this property by exposure to the air. It dissolves in concentrated sulphuric acid with a green colour; water separates it from this solution in rosy flakes. Distilled alone in a retort, it first parts with adherent water, and then with some oil having the odour of asafœtida. At the same time it froths considerably, and disengages sulphuretted hydrogen. As soon as the whole of the water has passed over, it turns dark brown and boils quietly.

The oils which distil over are green, blue, violet and red; have a more or less aromatic odour; and impart a yellow colour to dilute caustic potash, with which they are washed, and become turbid. The violet portion is the most remarkable in this respect; it parts with an oil to caustic potash, which gives this an intense red colour by exposure to the air. In the potash liquid with which these oils had been washed, only traces of formic and acetic acids could be detected.

The *gum* forms a white mass, which is gray and like horn when dry; among the products of its dry distillation only formic and acetic acids could be detected. The sulphuretted hydrogen which is disengaged in this operation is undoubtedly derived from the gypsum which always occurs in asafœtida.—Liebig's *Annalen*, lxxi. p. 23.

Method of separating Silver from Cupreous Solutions.
By M. Bolley.

The author mixes the solution with cane-sugar and potash or ammonia, boils, and extracts any precipitated oxide or protoxide of copper with acetic acid. The silver is obtained in this operation as a mirror, and sometimes also in the form of a powder—*Jahrb. für Prakt. Chem.*, xviii. 384.

On Papaverine. By G. Merck.

The name papaverine has been assigned by the author to the new and well-characterized alkaloid discovered by him some short time ago in opium*. According to the following investigation, its composition is represented by $C^{40}H^{21}NO^8$.

It is obtained by precipitating the aqueous extract of opium with soda, exhausting the precipitate with alcohol, and evaporating to dryness the brown tincture obtained. The residue is treated with dilute acid, the liquid filtered and precipitated by ammonia, when a resinous matter is obtained which contains the papaverine.

To procure it in a pure state, the resinous mass is dissolved in dilute muriatic acid, and mixed with acetate of potash. Another resinous precipitate is obtained, which after being washed with water is treated with boiling æther. From this solution the papaverine crystallizes on cooling.

This alkaloid may be prepared in a still more simple manner from the first dry resin. When mixed with its weight of alcohol, a smeary syrupy mass is formed, which on standing for several days at a temperature of 88° F. congeals to a paste of crystals. This is strongly pressed, and purified by recrystallization from alcohol and digestion with animal charcoal. The papaverine is treated with hydrochloric acid, to remove some narcotine which it still contains, and set aside to crystallize, when the sparingly-soluble readily-crystallizable hydrochlorate of papaverine separates, and the whole of the narcotine can now be removed by washing with cold water.

Papaverine separates from alcohol in a confused tissue of white acicular crystals, which are sparingly soluble in cold alcohol and æther, dissolve more abundantly on the application of heat, and separate again on the cooling of the solutions. It is insoluble in water. The solutions of papaverine turn slightly-reddened litmus-paper blue. When moistened with concentrated sulphuric acid, it acquires a dark blue colour, by which it is easily recognized.

The papaverine used for analysis was prepared from the pure muriate, which had crystallized from the aqueous solution, by dissolving it in hot water, precipitating with ammonia, and crystallizing the precipitate from alcohol. The analyses furnished—

Carbon	70·68	70·47	70·62	
Hydrogen	6·65	6·32	6·65	
Nitrogen	..	..	..	4·75

These numbers, with the assistance of those obtained in the analysis of the platinum double salt, lead to the following formula for papaverine:—

	Mean of Experiments.			
Carbon	70·59	40 = 240		70·79
Hydrogen	6·50	21	21	6·20
Nitrogen	4·75	1	14	4·13
Oxygen	..	8	64	18·88

Muriate of Papaverine, $C^{40}H^{21}NO^8 + HCl$.—Papaverine dis-

* See Chem. Gaz., vol. vi. p. 309.

solves readily in dilute muriatic acid, and falls on the addition of an excess of acid in the form of a heavy thick liquid, which collects at the bottom of the vessel. When left undisturbed for some time, crystals form in this oily layer and in the supernatant acid solution. By dissolving this first crop of crystals in boiling water, and letting the solution stand for several days, perfectly pure crystals of the muriatic salt are obtained; they are right rhombic prisms. Analysis furnished—

Carbon	63·40	63·83	64·00	
Hydrogen	5·97	6·09	6·17	
Chlorine	..	..	..	9·42

Whence we obtain the formula above given as follows:—

	Mean.			
Carbon	63·74	40	= 240·0	63·91
Hydrogen	6·07	22	22·0	5·86
Nitrogen	..	1	14·0	3·72
Oxygen	..	8	64·0	17·04
Chlorine	9·42	1	55·3	9·48

Platino-chloride of Papaverine, $C^{40}H^{21}NO^8, HCl + PtCl^2$.—Muriate of papaverine furnishes a yellow pulverulent precipitate with chloride of platinum, which is insoluble in water and in alcohol. It was washed with water, and dried at 212°. From the mean of several accordant analyses, the following composition was obtained:—

Carbon	43·71	40	= 240·0	44·02
Hydrogen	4·55	22	22·0	4·04
Nitrogen	..	1	14·0	2·57
Oxygen	..	8	64·0	11·74
Chlorine	..	3	106·5	19·53
Platinum	17·82	1	98·7	18·10

Nitrate of Papaverine, $C^{40}H^{21}NO^8 + NO^6H$.—The hot solution of the muriate, mixed with nitrate of silver, and filtered while hot from the precipitated chloride of silver, deposited the nitrate of papaverine in crystals on cooling. It gave on analysis—

Carbon	60·94	40	= 240	59·70
Hydrogen	6·21	22	22	5·47
Nitrogen	..	2	28	6·97
Oxygen	..	14	112	27·86

Products of Decomposition.—The nitrate is readily decomposed, and cannot be prepared by dissolving the base in nitric acid. When papaverine is boiled with moderately-concentrated nitric acid, the whole solidifies to a yellow crystalline mass. This compound is apparently formed from papaverine by the substitution of 1 equiv. hyponitric acid for 1 equiv. hydrogen. Other oxidizing agents, which do not effect any substitution, behave differently. Thus on boiling papaverine with peroxide of manganese, sulphuric acid and water, it became brown after some time; and in the course of a few hours, brown crystalline flakes separated; they were collected upon a filter, and washed with water, in which they gradually and almost entirely dissolved. Upon the addition of sulphuric acid, they were

again separated from the aqueous solution. Washed with a little water and pressed between blotting-paper, they formed a brown, silky, crystalline mass, which dissolved in boiling alcohol, but crystallized very imperfectly from it.

Papaverine has not the violent effects of morphine or the other vegetable alkaloids; pretty considerable quantities may be taken without injurious consequences.—Liebig's *Annalen*, Jan. 8, 1850.

Method of preparing Theine. By H. Heijnsius.

Stenhouse has recommended the preparation of theine from the extract of tea according to Mohr's method. The following is still more simple:—Old, spoiled tea is placed in an iron pot, which is covered with filtering-paper, and the whole then covered with a cylindrical paper cap. The temperature is now cautiously and gradually raised, when a sufficient quantity of pure theine will be found to have collected on the paper.—*Scheidk. Onderzoek.*, part v. p. 318.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Feb. 18, 1850. (The President in the Chair.) The following papers were read:—

"Researches on the Organic Radicals. No. II. Amyle," by Dr. E. Frankland.

Iodide of amyle, exposed in sealed tubes to a temperature of about 180° C., was acted upon by zinc with great difficulty; but by using an amalgam of this metal, the decomposition was effected with considerable rapidity at 160° C. The products of this decomposition were iodide of zinc and a colourless pellucid fluid, which last, by distillation in a water-bath and subsequent rectification, was separated into two portions, one boiling at from 30° to 35° C., and the other at 155° C. The latter was found to be perfectly pure amyle, yielding the formula $C^{10} H^{11}$. Amyle is a colourless pellucid liquid, possessing a slight ætherial odour and a burning taste. At −30° C. it becomes thick and oily, but does not solidify; its specific gravity in the liquid form is 0·7704 at 11° C.; that of its vapour, 4·9062. Hence it contains 5 vols. carbon vapour and 11 vols. hydrogen condensed to 1 vol.; and is thus, in this respect, perfectly analogous to methyle, ethyle and valyle. Amyle boils at 155° C.: it is only inflamed by an ignited body when previously heated, and it then burns with a bright smoky flame. It is insoluble in water, but miscible in all proportions with alcohol and æther. It is not affected by fuming sulphuric acid, and is only very slowly oxidized by boiling fuming nitric acid.

The remaining volatile product of the decomposition of iodide of amyle by amalgamated zinc was found to consist of two bodies having the empirical formulæ $C^5 H^5$ and $C^5 H^6$; but from the ana-

logy of the first to the compounds belonging to the olefiant gas series, the author considers its true formula to be $C^{10}H^{10}$, and proposes for it the name valerene; whilst he regards the second as a compound of 1 equiv. hydrogen with 1 equiv. amyle, giving it the formula $C^{10}H^{11}H$, and the name hydruret of amyle. Valerene is a colourless and transparent liquid, possessed of a peculiarly penetrating and disagreeable odour, much resembling that of butyrene. Its boiling-point is about 35° C.; it is rapidly and perfectly absorbed by anhydrous sulphuric acid. Hydruret of amyle is a transparent, colourless and exceedingly mobile fluid, possessing an agreeable odour resembling that of chloroform; it is the lightest liquid known, its specific gravity being only 0·6385 at 14°·2 C. Hydruret of amyle is insoluble in water, but soluble in alcohol and æther; it retains its fluidity at −24° C., and boils at 30° C.; its vapour burns with a pure white flame of surpassing brilliancy and devoid of smoke; it is not in the least affected by fuming sulphuric acid; it is a remarkably stable compound, and is only acted upon with great difficulty by the most powerful reagents.

The author thinks that hydruret of amyle exists in the most volatile portions of coal-tar, and that, by some simple modifications in the gas-manufacturing process, this substance, which would be invaluable for illumination, might be procured in large quantities at a moderate cost. The occurrence of hydruret of methyle (light carburetted hydrogen) also leads him to expect that the intervening members of the series, viz. hydruret of ethyle, hydruret of butyryle and hydruret of valyle, will be found in coal-gas, and that much of the illuminating power of that gas depends upon the presence of these compounds, the production of which, and their *non*-absorption during the purifying processes, must be a problem of considerable importance to the gas manufacturer. In addition to the bodies already described, iodide of amyle, when decomposed by zinc, yields zincamyle, $C^{10}H^{11}Zn$, a compound having properties quite analogous to zincmethyle and zincethyle.

The author's views on the rational constitution of the bodies belonging to these series are,—1st, that the radicals of the series to which methyle, ethyle, amyle, &c. belong possess exactly the chemical character and relations of hydrogen, than which however they are less electro-positive; 2nd, that these radicals can replace hydrogen in every combination in which this element plays the part of a simple radical, and is not enclosed in a group, which itself performs the functions of a simple body; 3rd, that the haloid compounds of these bodies may be regarded as hydracids, in which hydrogen has been replaced by one of these radicals; 4th, that the replacement of hydrogen in ammonia by these radicals renders the assumption of the hypothetical radical amidogen superfluous; 5th, that these radicals, in addition to the property of combining with electro-negative elements, possess also the faculty of uniting with hydrogen to form hydrurets.

"On some of the Salts of Chromic Acid," by Mr. J. Danson.

THE CHEMICAL GAZETTE.

No. CLXXIX.—April 1, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Contributions to the Doctrine of the Identity of the Sulphurous and Nitrogenous Animal and Vegetable Substances. By F. KELLER.

THE author has examined the products of oxidation of gluten by manganese and sulphuric acid. The identity of gluten in regard to its elementary composition with that of animal fibrine induced the author to take up this investigation; and the result has shown that the same products originate in this reaction as were obtained by Guckelberger* in the oxidation of fibrine and caseine.

20 lbs. of fresh gluten from wheat were gradually decomposed by adding to about 2 lbs. of concentrated sulphuric acid so much gluten at a time that no blackening occurred, and then so much water that none of the substance in solution separated in fine flakes. The mixture was then subjected to distillation with the addition of $2\frac{1}{2}$–3 lbs. of manganese in a capacious retort, and great care taken in cooling the highly volatile products given off. The evolution of gas is extremely violent, especially at the commencement, and requires constant watching. The products of distillation have a penetrating odour, causing a flow of tears and irritating the lungs to coughing. They strongly and permanently redden blue litmus-paper. The gases which are given off may be wholly condensed. The crude distillate was collected in large flasks, and mixed with powdered chalk to separate the acids, and the supernatant, transparent, neutral liquid distilled to separate the lime salts from the non-acid products. The residue was concentrated on the water-bath, and the lime salts converted into soda salts by the addition of carbonate of soda. That which had passed over was concentrated by repeated distillation until a milky liquid was obtained, upon which floated a layer of yellowish-coloured oil.

In separating these products, the lime salts were found to contain acids of the series $(C^2 H^2)^n O^4$, which were isolated according to the method recently described in these pages by Prof. Liebig†.

The liquid distilled from the lime salts had all the properties of an aldehyde. Concentrated caustic potash caused the production of resin; solution of silver gave, under the usual circumstances, a bright metallic mirror, and acidification soon resulted on exposure to the air. To separate the adherent water, the liquid was repeat-

* See Chem. Gaz. vol. vi. pp. 89, 114.

† Chem. Gaz., p. 24 of the present volume.

edly rectified; the aldehydes which passed over had mostly a somewhat yellowish colour; in the water remaining in the retort floated some drops of a heavy oil, which required much water for their volatilization. This last portion of the distillate possessed in a high degree the odour of the oil of bitter almonds. The mixture was separated by fractional distillation, and the portions collected as they passed over in the following order:—

I. between 73° F. and 104°.
II. between 104° F. and 140°.
III. between 140° F. and 176°.
IV. between 176° F. and 212°.
V. between 212° F. and 392°.

I. and II. consisted principally of the aldehyde of acetic acid. III. appeared to contain the aldehyde considered by Guckelberger to be that of metacetonic acid. IV. and V. contained the aldehyde of valerianic acid, $C^{10}H^{10}O^2$. The oil which passed over last was, as already hinted, oil of bitter almonds.

The nitryles of this series of compounds could not be formed, owing to the excess of free acid. The residue, consisting for the greater part of protosulphate of manganese, furnished, on distillation with a thin paste of lime, a considerable amount of ammonia; the peculiar odour of the distillate led the author to suspect the presence of volatile bases. Neutralized with oxalic acid, crystals of a salt separated, which dissolved in alcohol with the exception of traces of a substance with which no experiments could be made. The volatile acids obtained by decomposing the lime salts and the several aldehydes, compared with those which were obtained from fibrine and caseine, are contained in the following table:—

Products of oxidation of animal caseine, fibrine and albumen.		Products of oxidation of vegetable fibrine.
Aldehyde of acetic acid ..	$C^2\ H^4\ O^2$	Aldehyde of acetic acid
Aldehyde of butyric acid..	$C^8\ H^8\ O^2$	
	$C^{10}H^{10}O^2$	Aldehyde of valerianic acid
Formic acid.....	$C^2\ H^2\ O^4$	Formic acid
Acetic acid	$C^4\ H^4\ O^4$	Acetic acid
Metacetonic acid.....	$C^6\ H^6\ O^4$	Metacetonic acid
Butyric acid.....	$C^8\ H^8\ O^4$	Butyric acid
Valerianic acid	$C^{10}H^{10}O^4$	Valerianic acid
Caproic acid	$C^{12}H^{12}O^4$	
Benzoic acid	$C^{14}H^6\ O^4$	Benzoic acid
Oil of bitter almonds	$C^{14}H^6\ O^2$	Oil of bitter almonds.

Liebig's *Annalen*, lxxii. p. 24.

On the Composition of the Fæces of Man in Health and in Diabetes Mellitus. *By* John Percy, M.D., F.R.S.

[Continued from p. 107.]

Proximate Analysis of the Fæces in Health (No. 1. p. 103).—A portion of the same fæces as subjected to *ultimate* analysis was employed. By desiccation over the water-bath, a light brown residuum was obtained, of which 34·45 grs. were weighed for analysis.

1. *Matter soluble in Æther.*—The fæces were treated with æther (free from alcohol) until everything soluble in that menstruum was removed, and the æther at last came off quite colourless and without any fæcal odour. The æther was distilled off, and the residuum left *in vacuo* over sulphuric acid during several days ; it weighed 4·12 grs. ; it had precisely the appearance of fat, and was brownish-yellow.

2. *Matter soluble in Alcohol of spec. grav.* 830°.—The matter insoluble in æther was digested with successive portions of alcohol. The solution, which was clear and brown, was evaporated over the water-bath, and afterwards *in vacuo* over sulphuric acid, during several days. The residuum weighed 4·80, and left by incineration 0·48 of saline matter; a copious smoky flame was produced, and the odour of burnt horn was evolved.

3. *Matter soluble in Water.*—The matter insoluble in æther and alcohol was treated with successive portions of water at the ordinary temperature until the water ceased to acquire any perceptible colour. A clear deep brown solution was obtained, which by evaporation to dryness left a transparent, shining, deep brown matter, having an odour somewhat like that of extract of liquorice. After drying many hours in warm air, it weighed 4·76 grs., and by incineration gave of ash 0·76 grs. During incineration it frothed up much, like the residuum of diabetic urine, and emitted the odour of burnt horn.

4. *Fixed Saline Matter.*—50·13 grs. of dry fæces gave of ash 8·21. After washing with hot distilled water, 5·82 of insoluble ash remained. Soluble salts $=8·21-5·82=2·39$.

Examination of Saline Matter soluble in Water.

a. The solution slowly restored the colour of red litmus-paper.

b. A just perceptible trace of effervescence by the addition of *acetic acid* to the concentrated solution (*carbonic acid*).

c. By addition of nitrate of silver, a curdy white precipitate, insoluble in nitric acid (*chlorine*).

d. By addition of chloride of barium, a white precipitate, insoluble in dilute nitric acid (*sulphuric acid*).

e. By addition of nitrate of silver to the aqueous solution of the saline residuum (3.), a copious lemon-yellow precipitate, completely redissolved by nitric acid (*phosphoric acid*).

f. By addition of bichloride of platinum, a precipitate slowly deposited (*potash*).

g. By testing the dry salt before the blowpipe *carefully* and *comparatively*, very distinct yellow flame, but purplish at the origin (*soda*).

h. By evaporating, *even slightly*, the solution became milky ; and by continuing the evaporation further, a *white precipitate* was produced, which was instantly dissolved by *acetic acid* without the slightest effervescence ; and by the addition of oxalate of ammonia to the acid solution, turbidity was occasioned. These facts would seem to indicate the presence of *sulphate of lime*.

Saline Matter insoluble in Water.

a. Moistened red litmus-paper placed upon the salt immediately became blue (*lime?*).

b. Added acetic acid, and evaporated to dryness; to dry residuum added a small quantity of water; filtered, and to filtrate added oxalate of ammonia; after a short time a slight precipitate appeared, sufficient merely to produce milkiness, not removed by acetic acid (*lime*, in minute quantity).

c. Digested insoluble saline matter with nitric acid at a gentle heat; remained undissolved a small quantity of gritty matter, which examined by a lens was seen to consist of minute, irregular and colourless grains, like *common sand* (*silica*).

d. Filtered solution (*c.*); filtrate not perfectly bright; copious white precipitate by addition of excess of ammonia, and, with the *exception of some light gray flocculi*, redissolved by excess of acetic acid.

e. To solution (*d.*), after addition of excess of acetic acid, added oxalate of ammonia; copious white precipitate immediately (*lime*).

f. To solution (*c.*) added hydrosulphate of ammonia; blackish-green flocculent precipitate. (From reactions (*d.*) and (*f.*), *phosphate of iron?*)

g. By addition of chloride of barium and dilute nitric acid to solution (*c.*), no precipitate (*no sulphuric acid*).

h. To solution (*e.*), after standing and filtration, added ammonia in excess; copious and characteristic crystalline precipitate of phosphate of magnesia and ammonia (*magnesia*).

Analysis.

Organic matter soluble in æther	11·95
Organic matter soluble in alcohol of 830°	10·74
Organic matter soluble in water	11·61
Organic matter insoluble in these menstrua.....	49·33
Fixed saline matter *soluble* in water	4·76
Fixed saline matter *insoluble* in water	11·61
	100·00

The whole of the error falls, as usual in analyses of this kind, upon the insoluble organic matter. By alcohol of 830°, 1·39 per cent. of saline matter was removed; and by water, 2·20 per cent., free from chlorine, and consisting chiefly, if not entirely, of alkaline phosphates. The sum of these is 3·59; but the proportion of soluble saline matter obtained from the ash of 50·13 of fæces was 4·76. Now 4·76 − 3·59 = 1·17, which proves either an error of that amount, or that without incineration the soluble saline matter could not be perfectly removed, or that the two portions of fæces used in the proximate analysis and for the determination of the ash respectively, were not exactly uniform in composition.

Examination and Proximate Analysis of Flint's *Fæces* (No. 4).—The fæces were passed early in the morning, every precaution having been taken to prevent the admixture of urine. Colour, dark

brown; consistence, moderate. Desiccation was effected on a large flat dish in the hot-air chamber of the sand-bath.

1. *Examination with a view to the Detection of Sugar.*—200 grs. of the powder of the dried fæces were digested with alcohol of spec. grav. 832° at a little below the boiling-point. A dark brown solution was obtained, having an odour like that of fresh gall-stones. Thin whitish layers of apparently crystalline matter appeared on the surface on cooling. By evaporation over the steam-bath was left a dark brown liquid, which had the consistence of syrup, and became when cold hard like resinous matter. This was treated with hot water and filtered. The solution passed through very slowly, yet perfectly bright; it was clear, and had a dark brown colour. It was mixed with fresh yeast, and introduced into a graduated tube over mercury, which was left in a warm place till the following morning, when no gas was evolved. The precaution was taken to place by the side of the tube another tube, containing a portion of the same yeast mixed with water. In the last case only a very minute quantity of gas was disengaged. Now, to ascertain whether there might be present any substance derived from the fæces capable of retarding or preventing the action of yeast upon sugar, a minute fragment of cane-sugar was introduced through the mercury, and the apparatus was again put in a warm place. Fermentation speedily followed, as proved by the accumulation of gas at the top of the tube. Hence it may be concluded that sugar did not exist in these fæces.

2. *Examination in respect to Fatty Matter.*—200 grs. of the dried fæces were treated with a fluid ounce of boiling æther and filtered. Filtration proceeded slowly. By spontaneous evaporation, a light yellowish-green fatty matter was obtained, having a strong biliary odour, or at least the odour of gall-stones.

The residuum of the alcoholic extract insoluble in water (1.) was treated with warm æther. The ætherial solution was decanted and evaporated. The residuum was digested with a hot solution of potash, in order to dissolve out any resinous or fatty matter from cholesterine which might be present. By the action of the potash was obtained a tenacious mucus-like mass. This was washed with cold water, and then carefully pressed between linen in bibulous paper by the screw-press. Only a very small quantity of matter remained adherent to the linen, so that sufficient could not be detached for accurate examination. The piece of linen itself was then digested in hot æther, and the ætherial solution, which was colourless and exhaled a somewhat biliary odour, decanted into a glass capsule. By evaporation was left a white fat-like matter, which, examined carefully under the microscope, presented no trace of crystallization.

3. *Examination of the Ash.*—A portion of the fæces which had been well treated with alcohol was incinerated. The odour of burnt horn was evolved. The residuum was a mixture of white and red particles, and the intensity of the red colour excited some surprise. It was treated with water, which only partially dissolved it.

Aqueous Solution.

a. Immediately restored the colour of red litmus-paper.

b. No effervescence on the addition of hydrochloric acid (no *carbonic acid*).

c. Yellowish precipitate by addition of nitrate of silver, entirely redissolved by nitric acid (*phosphoric acid*).

d. As the extract which had been well treated by alcohol was employed for incineration, the chlorides must have been removed.

Solution by Nitric Acid of Matter insoluble in Water.—Precipitate with chloride of barium, partially redissolved by nitric acid (*sulphuric* and *phosphoric acids*).

The examination was not further proceeded with.

Re-examination of the fixed Saline Matter of these Fæces.—After again drying during several hours between 100° and 110° Cent., 61·01 grs. were weighed. As the fæces always emitted during the drying a strong odour, as the same quantity had been dried several times, and as some matter had evidently condensed upon the inner surface of the small copper drying-oven, it is to be expected that the per-centage of ash would be somewhat greater in this determination than in the preceding one. Accordingly it will be seen that there was a difference of excess, although very slight. By incineration fœtid gas was copiously evolved, and burned with a smoky flame, like that produced by the combustion of tallow; and at first some brownish oily matter condensed around the edge of the platinum crucible. The ash, which had a light brown colour, weighed 5·71 =9·36 per cent. Stallard obtained 9·26 and 9·35. The platinum crucible was slightly attacked. The ash was washed with hot water until the wash-water ceased to be affected by nitrate of silver. The salts *soluble* in water, as determined by loss, amounted to 2·59; the salts *insoluble* to 3·12; or, salts soluble in water, 45·35 per cent.; and insoluble, 54·65.

(*By* Stallard).—3·37 grs., washed with boiling water until wash-water ceased to be affected by nitrate of silver, gave of saline matter soluble in water, 1·51, of which alcohol of 830° spec. grav. removed 0·26; and of insoluble, 1·86. Or, salts soluble in water, 44·80 per cent.; and insoluble, 55·20. Of the former, 7·71 were soluble in alcohol of 830°, and 37·09 insoluble.

Examination of the Aqueous Solution of the Soluble Salts.

a. By reducing the volume of the solution by evaporation, a few white flocculi separated, which would probably have been inappreciable by the balance.

b. By addition of acetate of baryta, a very copious white precipitate was produced, which was in great measure redissolved by addition of a few drops of nitric acid. The usual analytical precautions having been observed, 0·31 of sulphate of baryta was obtained.

c. To solution (*b.*), after separation of sulphate of baryta, nitrate of silver with nitric acid were added; 0·69 of chloride of silver was obtained.

Saline Matter insoluble in Water.

a. It was moistened with water, and then nitric acid was added. There was slight effervescence. It was digested, filtered, and washed with water containing nitric acid. The solution was evaporated to dryness, and heated to redness. Orange fumes were evolved. The residuum had a pale brown colour, and weighed 2·58. The insoluble matter left upon the filter, as determined by incineration, weighed 0·29. 2·58 + 0·29 = 2·87. But, 3·12 (the amount of insoluble saline matter given before) − 2·87 = 0·25 difference.

b. The residuum (*a.*), obtained by evaporation of the acid solution and subsequent heating to bright redness, was broken up and treated with a small quantity of water; red litmus-paper was instantly turned blue by this solution.

c. It was digested with acetic acid, and evaporated to dryness at a gentle heat. This product was washed with boiling water on a very small filter, and the solution evaporated to dryness, during which the residuum was accidentally carbonized. It was then heated to redness, when the odour of a burning acetate was evolved. Finding that the carbon could not readily be removed by incineration, a few drops of nitric acid were added, which occasioned effervescence. The whole was evaporated to dryness, and again heated to redness, when there remained a perfectly white product. This was heated with sulphuric acid in excess, evaporated to dryness, and heated to redness. The residuum weighed 1·78 gr. It was treated with acetic acid, and to the filtered solution oxalate of ammonia was added, when a white precipitate was immediately produced.

d. To residuum (*c.*), insoluble in acetic acid, hydrochloric acid was added, which readily dissolved it, forming a yellowish solution, like dilute sesquichloride of iron. This solution was treated with excess of ammonia, which occasioned a copious white precipitate. This was redissolved by an excess of acetic acid, with the exception of some grayish flocculent matter, which on standing subsided. The whole was then boiled, but still this insoluble matter remained. The solution was filtered. When dry, the substance upon the filter had a pale brown tinge. It was dissolved in dilute nitric acid; ammonia added in excess to this solution precipitated gray flocculi, which became deep greenish-black by the addition of hydrosulphate of ammonia. Some of the acid solution was tested with chloride of barium, but no trace of sulphuric acid was found. It may be inferred that the flocculent matter insoluble in acetic acid was *phosphate of sesquioxide of iron*. A precipitate, having precisely the same appearance and giving similar reactions, was obtained by mixing dilute solutions of sesquichloride of iron and common phosphate of soda.

e. To the acetic acid solution (*d.*) oxalate of ammonia was added, which immediately produced a copious white precipitate (*lime*).

f. The solution (*e.*) was allowed to stand some time after addition of oxalate of ammonia, and then filtered. To the filtrate ammonia in excess was added, when the characteristic precipitate of phosphate of magnesia and ammonia shortly appeared. On the addition of

hydrosulphate of ammonia only the slightest brown tinge was produced.

Proximate Analysis of the same Specimen of Flint's *Fæces as used in the foregoing Experiments.*—After drying as before, 15·63 grs. were weighed.

1. *Matter soluble in pure Æther.*—A pale brown solution was obtained, having a strong feculent odour, somewhat resembling that of hot strong solution of common glue. At first the matter was simply macerated with cold æther in a stoppered bottle; the whole was frequently shaken, and the æther allowed each time before decanting the supernatant solution to remain in contact with the fæces many hours. This treatment was repeated five times with æther, and twice of the five times under slight pressure, until at last the æther came off having only a very slight odour and a just perceptible tint. Each time the ætherial solution was passed through a filter. The æther was evaporated, and the residuum exposed *in vacuo* to sulphuric acid during many hours. The evaporation of ætherial solutions of this kind requires considerable care to avoid loss by the solution escaping over the sides of the vessel. A minute quantity of fatty matter was so lost in this analysis. The residuum weighed 3·44.

Examination of this Residuum.—It was digested with a solution of potash during many hours on the sand-bath at a very gentle heat. A clear pale brown solution was obtained, with some colourless flocculent matter floating in it; it had only a feeble odour, much like that of caustic ley alone. Hydrochloric acid in excess was added, when copious, pale yellowish-gray, curdy flocculi separated; and again immediately the true biliary or fæcal odour was perceived, though it was not strong. The solution was filtered. The filtrate had only an extremely faint straw tinge, and did not evolve a *very distinct* fæcal odour. The residue on the filter was washed with a small quantity of cold water, the filter pressed slightly between bibulous paper; the pale yellowish-brown mass thus obtained was transferred to a capsule, and hot water poured upon it, when it immediately melted, and appeared on the surface of the water as a dark brown oil, exhaling only a feeble odour even while melted. A small quantity of this fat, heated in a test-tube over a spirit-lamp, evolved offensive products, apparently similar to those produced by fats in general when so treated. The filter containing the light flocculent matter, insoluble in solution of potash as above mentioned, was washed with water, the filter pressed between bibulous paper, and boiled with adherent matter in æther; the ætherial solution by spontaneous evaporation yielded a minute quantity of white matter, in which however under the microscope I was unable to detect any distinct appearance of crystallization.

2. *Matter soluble in Alcohol of* 820°.—Residue (1.), insoluble in æther, was digested several times with alcohol at a gentle heat. The solution at first had a deep brown colour. The treatment with alcohol was continued until the latter came off with the slightest perceptible colour. By evaporation a deep brown matter was ob-

tained, exhaling a slightly fæcal or biliary odour. It was dried in the water-bath during many hours.

The residuum of organic matter, as determined by loss from incineration, weighed 1·74.

3. *Matter soluble in Water.*—I proceeded precisely as in the former analysis. A bright deep brown solution was obtained, which, by evaporation and subsequent drying during many hours, gave a deep brown brittle extract, weighing 1·88. The treatment with successive portions of water was continued until the water passed through the filter colourless. By incineration the extract evolved the odour of burnt horn, and gave of saline matter 0·54. The organic matter therefore is 1·88−0·54=1·34.

Analysis.

Organic matter soluble in æther		22·00
Organic matter soluble in alcohol		11·13
Organic matter soluble in water		8·57
Organic matter insoluble in these menstrua		48·93
Saline matter soluble in water, and containing—		
Chlorine	0·27	4·24
Sulphuric acid	0·23	
Phosphoric acid, Alkaline bases	3·74	
Saline matter insoluble in water, but soluble by the addition of nitric acid		4·64
Matter insoluble in nitric acid		0·47
		100·00

Examination of Flint's *Fæces in respect to Fatty Matter, while he was taking 3 oz. of Bacon daily.*—A portion of the same fæces as used in the ultimate analysis No. *5* was employed. 39·92 grs., treated with æther in the usual way, gave of fatty matter 20·58 =51·55 per cent. The residuum, after evaporation of the æther, was dried *in vacuo* over sulphuric acid. In this determination there was a slight *error of loss*, owing to the great difficulty in filtering the ætherial solution, which contained minute particles in suspension.

Examination of the child Stubbs' *Fæces, No. 3 of the table.*

Matter soluble in pure Æther.—I proceeded precisely as in the former analyses, continuing to treat with æther until it came off without the slightest colour or odour. 76·58 grs. gave of fatty matter 12·38=16·16 per cent. This fat seemed to consist of not less than two fatty bodies, one more liquid than the other at the ordinary temperature. I made three ultimate analyses of it, but the results varied considerably, and I was almost disposed to infer that the variation was in some measure owing to the want of uniformity of composition even in two or three portions taken consecutively from the same quantity, for on careful inspection it appeared to consist of irregular grains mixed with a brown oil. I give the results of the analysis in which I obtained the largest per-centage

of carbon and hydrogen, as being probably the nearest approximation to the truth. Chromate of lead was used as the oxidizing body. 3·396 grs. gave of HO, 4·00=H 13·07 per cent.; of CO^2, 10·14 =C 81·42. If nitrogen were absent, the composition would be as follows:—

Carbon	81·42
Hydrogen	13.07
Oxygen	5·51
	100·00

This fat therefore in composition approximates to cholesterine, but much more nearly to a crystalline product obtained from the brain, and analysed by Dr. R. D. Thomson (Liebig, Tr. de Chim. Org., vol. iii. p. 318), whose analysis I insert for the sake of comparison:—

	Product of the brain, by Dr. Thomson.		Fat of the fæces, by J. P.
Carbon	81·9	81·51	81·42
Hydrogen	13·3	12·02	13·07
Oxygen	4·8	6·47	5·51
	100·0	100·00	100·00

Examination of Fixed Saline Matter of Stubbs' *Fæces.*—30·76 grs. of fæces gave of saline matter *soluble* in water, 0·74=2·41 per cent.; of *insoluble*, 5·44=17·68 per cent.

Saline Matter soluble in Water.

a. It slowly turned red litmus-paper blue.

b. By chloride of barium, a minute quantity of white precipitate, partially redissolved by nitric acid (*sulphuric and phosphoric acids*).

c. By nitrate of silver and nitric acid, slight milkiness. I was particularly struck with the small quantity of *chlorine* present.

d. By evaporation, small, distinct, prismatic crystals were obtained (*sulphate of lime?*).

e. By addition of bichloride of platinum to solution (*d.*) concentrated by evaporation, a tolerably abundant yellow granular precipitate (*potash*).

f. A little of the dry saline matter was tested before the blowpipe on platinum wire, with the precaution of making comparative trials with the wire alone and with phosphate of soda; but I did not satisfactorily detect soda in this instance. The pinkish tint at the origin of the flame, indicative of potash, was distinct, although I thought the end of the flame was slightly more yellow with the salt than with the wire alone.

g. By addition of nitrate of silver to the concentrated solution, instantly a curdy lemon-yellow precipitate (*phosphoric acid*).

h. A minute quantity of the white matter (*d.*) did not redissolve in water, but instantly dissolved by addition of acetic acid without effervescence; however, the quantity operated upon was very minute. By addition of oxalate of ammonia to the acid solution, instant turbidity, followed by a distinct precipitate.

Of the per-centage of Fat (matter dissolved by pure æther) in the Organic Constituents of the Fæces of the Man in Health, of the child Stubbs *and of* Flint, *or Numbers* 1, 3, 4 *and* 5 *respectively.*

No. 1.	14·28 per cent.
No. 3.	20·22 ...
No. 4.	24·27 ...

Concluding Observations.

The preceding investigation I admit to be very incomplete; but not having the intention of prosecuting the inquiry further, I have preferred publishing the results in their present state to withholding them altogether, as it is probable that some of them may not be uninteresting to chemists engaged in the study of animal chemistry. The nature and limits of the 'Chemical Gazette' forbid that I should enter upon any physiological or pathological discussion; so that in these concluding remarks I shall confine myself as much as possible to the strict chemistry of the subject.

1. As I have already stated, it is worthy of remark that the ultimate composition of the fæces would seem to be more uniform, even under different conditions of diet and exercise, than might have been anticipated. In proof of this I have alleged the close agreement between Dr. Playfair's analysis of the fæces of a soldier at Giessen and that which I have given of the fæces of a young man in this country. Besides, the ratio of the fixed saline matter of the fæces soluble in water to that which is insoluble in water, as given by Weber in H. Rose's paper "On the Inorganic Constituents of Organic Bodies" (Phil. Mag. vol. xxxv. p. 275), is nearly the same as that which I found. Thus, according to Weber, 100 parts contain of soluble matter 30·63, and of insoluble 69·37. The proportions which I have given in the proximate analysis of the fæces in health are 4·76 of soluble matter and 11·61 of insoluble, or 29·07 per cent. of the former and 70·93 of the latter.

2. *Of the Constituents of the Inorganic Matter of the Fæces in Health.*—The matter soluble in water contained carbonic acid, chlorine, sulphuric acid, tribasic phosphoric acid (*c*-modification, Rose), potash, soda and lime.

The matter insoluble in water contained phosphoric acid, lime, magnesia, iron, and silica as sand.

These results correspond, so far as they go, to those of Weber cited above.

3. *Of the presence of Sugar in the Fæces in Diabetes mellitus.*—M'Gregor states that sugar is "readily discoverable in the stools of diabetic patients;" but he appears to have founded that statement upon a single observation, and to have decided upon the presence of sugar from the gradual formation of crystals upon the surface of the fæces during spontaneous desiccation. He had taken the precaution of avoiding the presence of urine in the vessel which received the fæces. (Med. Gaz. vol. xx. p. 272.)

Now it is hardly necessary to remark, that this single observation

is quite insufficient to establish the general fact of the presence of sugar in diabetic fæces; but possibly even in the particular instance mentioned the observation may not be altogether decisive; for it is not impossible that M'Gregor, unless he had availed himself of other sources of proof, may have mistaken the crystals of phosphate of magnesia and ammonia, which are known to occur in fæces, for those of grape-sugar. (*Vide* Simon's Anim. Chem., Day's Trans., vol. ii. p. 366; Donné, Cours de Microscope, p. 484; Berzelius, Tr. de Chim., vol. vii. p. 269. Paris, 1833.)

In the only instance in which I sought for sugar in diabetic fæces I failed to detect it. Against that result the objection may be urged that sugar may have been present in the fæces at the time of their evacuation, and have been subsequently destroyed, or otherwise changed, by the process of desiccation. However, it does not seem probable that such destruction or change should occur under the circumstances. I would not propose to infer from this single observation the general *negative* fact of the absence of sugar from diabetic fæces, any more than I would the general *positive* one of its presenc in these fæces from the single instance of M'Gregor.

Simon searched for sugar in the fæces of a male diabetic patient, but without success. (Day's Trans., vol. ii. p. 377.)

From the preceding data, it may be concluded that the question of the *presence* or *non-existence* of sugar in diabetic fæces as a general fact remains undecided. Probably the truth will be found to be, that sugar may be present or not in the fæces in this disease according to circumstances. Thus, for example, if diarrhœa occur, and the urine be decreased in consequence, as I have known to be the case, it seems not unreasonable to suppose that some saccharine matter may be diverted from the kidneys, and pass off by the intestinal canal.

4. *Of the Composition of the Fæces in Diabetes mellitus.*—Simon has given a proximate analysis of the fæces of a male diabetic patient, whose daily ingesta consisted of 8 oz. of dry gluten bread, 11½ oz. dry meat, 2 oz. dry egg and 2 oz. cod liver oil. (Day's Trans., vol. ii. p. 377.) Now, while this analysis differs in some points from that which I have given, it agrees in one point, namely, the large proportion of fat, which amounted even to 34 per cent. In the case of Flint, it will be remembered the proportion of fat amounted to 59 per cent. of the organic matter, while he was taking about 3 oz. of fat bacon daily; at another time to 24 per cent.; and even in the case of the child Stubbs to 20 per cent.; while in the fæces of the healthy man it did not exceed 14 per cent. of the organic matter. If we take the proportion of hydrogen as a tolerably correct measure of the proportion of fatty matter, we shall find that the proportion of fatty matter is in every specimen of diabetic fæces, with the exception of No. 3, sensibly greater than in the fæces of health under very different circumstances of diet, and greater also than in No. 9, the fæces of the girl affected with jaundice. However, further observations are required to enable us to arrive at a satisfactory general conclusion on this subject.

Lehmann maintains that the "fæces of diabetic patients frequently yield a mere trace of nitrogen." (Note in Day's Trans., vol. ii. p. 377.) This is opposed to the results of Simon and myself. The odour evolved on incineration of diabetic fæces, so far as my observation has extended, has of itself uniformly afforded unequivocal proof that nitrogen is by no means deficient in these fæces. In one analysis the proportion of nitrogen amounted to 12 per cent.

With regard to the fixed saline matter of the fæces in Diabetes mellitus, a more extended and precise investigation is required to enable us to arrive at satisfactory conclusions upon the subject.

On the Products of Decomposition of Caffeine.
By Dr. Rochleder.

The author has ascertained, by further examination and comparison of the properties of the base (formyline) obtained in the decomposition of caffeine by chlorine, that it is identical with the methylamine, $C^2 H^5 N$, discovered by Wurtz. On comparing the numbers found by Rochleder in his analyses with those calculated, it will be found that the formula of methylamine may be deduced from them, especially with the assistance of a fresh analysis by the author, which gave 5·2 carbon and 2·62 hydrogen. The formula of the platino-chloride of methylamine corresponds to the following composition, by the side of which are arranged the results of Rochleder's analyses, and the numbers calculated according to the formula $C^2 H^4 N, ClH + PtCl^2$:—

Calculated.				Found by Rochleder.					
C^2	5·07	C^2	5·09	4·87	4·86				
H^6	2·53	H^5	2·12	2·49	2·49	2·42			
N	5·91	N	5·94						
Cl^3	44·91	Cl^3	45·08						
Pt	41·58	Pt	41·77	41·42	41·43	41·43	41·61	41·42	41·06

The composition of caffeine and the explanation of its mode of decomposition are corrected by the author assuming that the formula of caffeine, $C^{16} H^{10} N^4 O^4 = C^2 N, C^2 H^5 N, C^{12} H^5 N^2 O^4$. The chlorine destroys the $C^2 N$ in the presence of water; the methylamine, $C^2 H^5 N$, is obtained as hydrochlorate; and the group $C^{12} H^5 N^2 O^4$ assimilates 2 equivs. oxygen and 2 equivs. water to form amalic acid, $C^{12} H^5 N^2 O^4 + 2O + 2HO = C^{12} H^7 N^2 O^8$.

Cholestrophane, $C^{10} H^6 N^2 O^6$.—When, after the production of amalic acid, chlorine is continued to be passed through the decomposed caffeine, there is formed from the amalic acid the same body which Stenhouse obtained in treating theine with nitric acid, and called nitrotheine. Stenhouse found it to contain 5 equivs. carbon to 1 equiv. nitrogen, and 42·15 carbon, and 4·28 hydrogen. This substance possesses the greatest resemblance to cholesterine. According to Rochleder, it is no nitro-compound, but is a mere product of oxidation, in the present case by chlorine. From the above resemblance the author has assigned to it the name of cholestro-

phane. It is formed from amalic acid as follows:—$C^{12}H^7N^2O^6$, amalic acid $+G=C^{10}H^6N^2O^6+C^2HO^3$. When cholestrophane is boiled with potash, ammonia is disengaged, and the potash is found to be combined with an acid, which, after neutralizing the liquid with nitric acid, can be precipitated in the form of a white precipitate by nitrate of silver. The author reserves the examination of this substance for a future occasion. Cholestrophane furnished on analysis—

	Rochleder.	Stenhouse.			
Carbon	42·00	42·15	10 =	60	42·25
Hydrogen	4·25	4·28	6	6	4·22
Nitrogen	20·00	19·56	2	28	19·71
Oxygen	33·75	34·01	6	48	33·82

Liebig's *Annalen*, Jan. 1850.

On some Combinations of Phosphoric Acid with Alumina. *By* Dr. H. Ludwig.

The following are the results of the author's investigation:—

The precipitate which an excess of sesqui-*c*-phosphate of soda produces in a precipitate of potash-alum is not $1\frac{1}{2}$-phosphate of alumina, not even in the recently-precipitated hydrated state, but after sufficient washing with cold water, desiccation and ignition, has the formula $8Al^2O^3, 9PO^5$. It contains 39·385 per cent. of alumina and 60·615 per cent. phosphoric acid. Its formula corresponds to that of the $\frac{8}{9}$-phosphate of baryta and chloride of barium, and to that of the $\frac{8}{9}$-phosphate of lime.

By solution in hydrochloric acid, and precipitating the solution with caustic ammonia, the $8Al^2O^3, 9PO^5$ loses $\frac{1}{8}$th of its phosphoric acid, which remains in solution with a small quantity of alumina. The precipitate produced contains ammonia in the air-dried state; after calcination it presents the formula Al^2O^3, PO^5, and contains 41·64 per cent. alumina and 58·36 phosphoric acid. In the hydrated state, and disregarding the amount of ammonia, it possesses the composition of Gibbsite analysed by Hermann.

By dissolving the $\frac{2}{3}$-phosphate of alumina in hydrochloric acid, and decomposing the solution by an excess of acetate of soda at a boiling heat, a precipitate is formed, which in the calcined state presents either the formula Al^2O^3, PO^5 or $16Al^2O^3, 15PO^5$. $\frac{1}{8}$ to $\frac{3}{16}PO^5$ remains in solution, but the whole of the alumina is contained in the precipitate.

A solution of the $\frac{2}{3}$-phosphate of alumina in caustic soda, on being mixed at the ordinary temperature with acetic acid until it has a slight acid reaction, furnishes a precipitate, which after ignition has the formula $16Al^2O^3, 15PO^5$, and contains 43·4 per cent. alumina and 56·6 phosphoric acid.

The alumina is precipitated from a solution of the $\frac{2}{3}$-phosphate of alumina or of the Al^2O^3, PO^5 in caustic soda by a current of sulphuretted hydrogen or by an excess of sulphuret of ammonium as a

very basic phosphate, which dissolves more easily in acetic acid than the $8Al^2O^3, 9PO^5$ or the Al^2O^3, PO^5. A great portion of the phosphoric acid remains in solution.

The author is of opinion that for analytical purposes the $\frac{2}{3}$- or $\frac{15}{16}$-phosphate may be regarded as $\frac{1}{1}$-phosphate.—*Archiv der Pharm.*, lix. p. 19.

On the Constituents of Aristolochia Clematitis.
By F. L. Winckler.

The author gives the following preliminary notice respecting the volatile oil and the bitter substance contained in the root of *Aristolochia Clematitis*. The distilled oil, after depositing mucilage, is of a bright orange-yellow colour, becomes slightly heated when mixed with dry iodine, and soon becomes darker by exposure to the air with change of odour; it becomes soft and resinous, and then smells like a copaiva balsam. 4 lbs. of root furnished, on distillation by means of steam, 120 grs. of transparent oil.

The bitter substance was extracted from the residue of the root by water containing a little ammonia, and the solution mixed with dilute sulphuric acid, when nearly the whole of the bitter substance was precipitated in flakes. Alcohol of 0·863 dissolved this precipitate; the solution was nearly deprived of colour by animal charcoal, and left on evaporation an amorphous brownish-yellow residue, which was freed from resin by repeated solution in cold water. In this state the substance readily absorbed water, owing to the salts it contained; it dissolved readily in water and in alcohol, was insoluble in æther, and possessed an insupportably bitter taste. The author considers this substance to be identical with the bitter principle contained in *Rad. Serpentariæ* (from *Aristol. Serpent.*). This substance is neutral, is precipitated by basic acetate of lead and nitrate of silver, and exhibited in other respects no characteristic reactions.—*Jahrb. für Prakt. Pharm.*, xix. p. 71.

On the Chemical Composition of the Coats of Arteries.
By M. S. Schultze.

The middle arterial coat of the carotid of the ox was exhausted by treatment with cold water and water at 104° F., and pressure. The clear extract was slightly alkaline, not rendered turbid by ebullition, strongly precipitated by a small quantity of acetic acid, the precipitate soluble in a large quantity of acetic acid, and reprecipitated by ferrocyanide of potassium. The liquid filtered from the acetic precipitate was slightly acid, and gave a few flakes of coagulated albumen on boiling. The remaining liquid was not precipitated by ferrocyanide of potassium. The substance precipitated by acetic acid and redissolved by excess, was shown, by its reaction with other acids and metallic salts, and its coagulation by rennet, (on the addition of a little sugar of milk) to be caseine. When its solution was evaporated, a scum formed on the surface. It dif-

fered from Simon's caseine of the blood in not being coagulated by heat like globuline; nor did it contain any trace of hæmatine, which the globuline of the blood always does. The outer cellular coat of the arteries also contains a considerable amount of caseine, although in far less proportion. In the middle arterial coat of the carotid of the ox, the caseine amounted to 20·98 per cent. of the solid residue and to more than half of the matters soluble in water. Areolar tissue and the ligamentum nuchæ also contain traces of caseine. The membranes of the veins contain it in large proportion. The mean per-centage of water and solids found in the middle coat of the carotid amounted to—

	Carotid.
Water	71·17
Solids	28·83
	100·00

100 parts of the solid constituents of the fibres of the carotid consisted of—

Portions of the fibres insoluble in water	60·66
Salts insoluble in water	1·07
Caseine	20·98
Albumen	7·40
Extractive matter	7·43
Salts soluble in water	2·46
	100·00

The portions insoluble in water yielded a large amount of a proteine compound to boiling acetic acid and solution of potash. They consist of the contractile fibres, which are dissolved by these reagents, and the elastic fibres, which are unaffected.

The gelatine of the elastic fibre is with difficulty separated from those fibres which yield the proteine compound and those of the areolar tissue. This may however be effected by ebullition with solution of potash. By subsequent ebullition with water for thirty hours at a temperature of 320° F., they are dissolved. The solution does not gelatinize, is copiously precipitated by tannic acid, nitropicric acid, chromic acid, tincture of iodine and bichloride of mercury, whilst those reagents which precipitate chondrine do not affect it. Hence the gelatine of the elastic tissues is probably identical with gluten. —*Ann. der Pharm. und Chem.*, Sept. 1849.

On some Phænomena of Reduction: a new Method of separating Iron from its Compounds. By J. A. Poumarede.

Some years ago the author examined the action of some metals, and especially that of zinc, upon metallic solutions. On bringing together solutions of iron, cobalt, nickel and manganese, the decomposition of the water and the disengagement of hydrogen appeared to him not to be produced by the zinc, but by a certain quantity of the dissolved metal, precipitated by that antagonism which is always

exhibited when two different radicals occur in the presence of a limited amount of oxygen, coating the reducing metal, and producing in this manner a galvanic element. To demonstrate that such might really be the case, it was necessary to establish that this reaction, which might be expressed by the following equation, $2(Fe^2O^3, 3SO^3) + Zn^3 + HO = Fe^3O^3, 3SO^3 + Zn^3O^3, 3SO^3 + FeO + H$, might also take place in the following manner:—$2(Fe^2O^3, 3SO^3) + Zn^3 + HO = Fe^3O^3, 3SO^3 + Zn^3O^3, 3SO^3 + HO + Fe$.

The author succeeded, in fact, in doing this by quickly removing the precipitate of reduced metal from the zinc, and so preventing the formation of a galvanic circuit; instead of the hydrogen there now appeared a corresponding quantity of metallic iron. After further examination of these phænomena, the author has not attained the desired result in a scientific point of view; he has however discovered the following three methods for the reduction of iron:—

1. *Salts of the Protoxide of Iron*, under the above-mentioned circumstances, part with half their oxygen at a slight elevation of temperature, the corresponding amount of iron being separated in a metallic form. Such iron can be prepared at very little cost, and it will undoubtedly find some useful application in the arts. It is purer than the ordinary iron of commerce, has the usual colour, and all the other properties of iron, and the specific gravity of 7·50.

2. *Protochloride of Iron* may be reduced by zinc in the state of vapour. The iron so obtained is well adapted for the reduction of a number of other protochlorides; it always forms dendritic crystals, among which occur here and there hollow tetrahedra. Its specific gravity is 7·84, which is nearly the same as Broling assigns to iron melted into bars. Its purity is so great, that it decomposes water only imperceptibly in dilute sulphuric acid.

3. The carbon, whose influence the author had distinctly recognised in the previous reduction, has been especially examined as regards its reducing action, and application made of well-known facts, in which he assumes the views brought forward by Leplay and Laurent on cementation to be proved.

When peroxide of iron (colcothar) or protocarbonate of iron is heated with charcoal, the oxide of iron being packed in shallow sheet-iron vessels with intervening strata of carbon placed upon iron-wire sieves, in a cast-iron cylinder placed vertically in a reverberatory furnace, and the upper part of which is connected by a tube of sufficient length with the atmosphere or the requisite apparatus, and it is now heated to a red heat, there is observed during the entire operation a disengagement of carbonic oxide, which may be immediately employed for other reductions. The peroxide or protocarbonate of iron is converted into porous iron, which is not pyrophosphoric and has all the properties of a very pure iron.

To explain this behaviour, we must admit, according to Leplay and Laurent, that the atmosphere of the apparatus first produces with the carbon a quantity of carbonic oxide, which reacts upon a corresponding amount of peroxide of iron, and furnishes carbonic acid; this is next reduced by the charcoal to carbonic oxide, which

then constitutes twice the amount first present. In this manner, after a short time, the oxide is placed in a reducing atmosphere. By this method the author has reduced a number of other compounds, for instance the alkaline and earthy sulphates.—*Comptes Rendus*, xxix. p. 518.

ANALYTICAL CHEMISTRY.

On the Quantitative Estimation of Fluorine. By H. Rose.

Of the methods which have hitherto been employed for the estimation of fluorine, the best is still that of treating the fluorated substance with sulphuric acid, and so expelling the fluorine. From solutions the fluorine is mostly precipitated as fluoride of calcium. This method is one of the best, although not perfectly accurate; and its application is connected with difficulties, the precipitated fluoride of calcium frequently separating in a gelatinous state and stopping the pores of the filter. This can often be avoided by boiling the liquid with the precipitate. The precipitation may be made with chloride of calcium or by nitrate of lime. In the first case the precipitate contains no chloride. When the solution containing the fluorine is acid, it has generally been the practice to neutralize it with ammonia before adding the solution of lime; but this method leads to erroneous results, as the fluoride of calcium is soluble in ammoniacal salts. The acid solution must therefore be saturated with carbonate of soda, and then the solution of lime added. The precipitate, which contains fluoride of calcium and carbonate of lime, is calcined, then treated with acetic acid, the whole evaporated to dryness on the water-bath, the dry mass digested with water, and the fluoride of calcium collected on a filter and well washed.

From neutral solutions the fluorine may be separated completely as fluoride of barium or fluoride of lead, so that the amount of fluorine may be determined with accuracy. For the precipitation, either nitrate of baryta or nitrate of lead is used; the liquid is then mixed with an equal volume of strong alcohol, and the precipitate washed with alcohol. The fluoride of barium can be calcined, but not the fluoride of lead, as it is volatile like the chloride of lead; it is dried at 212°. But when the liquid containing the fluorine also contains chlorides, the precipitates contain chloride of barium and chloride of lead along with the fluorides.

When fluorine is present in insoluble compounds, and only in small quantity, it is frequently difficult to determine its amount by decomposing these compounds with sulphuric acid; the usual plan then is to decompose the compound by fusion with carbonated alkali. But several insoluble fluorides, for instance the fluoride of calcium, are not decomposed by fusion with carbonated alkali; they

melt, it is true, to a clear liquid; but if after cooling, the fused mass is treated with water, mere traces of alkaline fluoride are dissolved, and nearly the whole amount of the fluorine is contained in the insoluble residue. But if the fluoride of calcium is fused with carbonated alkali in the presence of silica, perfect decomposition takes place, an alkaline fluosilicate being first formed, which is decomposed by the excess of the alkaline carbonate. After cooling, the fused mass is treated with water, and the silica held in solution precipitated by carbonate of ammonia. The washed insoluble residue contains not a trace of fluorine; the whole amount is present as alkaline fluoride along with alkaline carbonate in the filtered solution, from which it can be precipitated by a lime salt as fluoride of calcium.

When phosphates, and especially the phosphate of lime, are present along with fluorides in insoluble compounds, they cannot be decomposed by fusion with carbonated alkali even with the addition of silica. If, on the other hand, the phosphoric acid is combined with alumina, perfect decomposition results, and the whole of the phosphoric acid, together with the entire amount of the fluorine and the excess of carbonated alkali, are contained in the solution obtained by treating the calcined mass with water, from which the minute traces of dissolved silica can be precipitated by carbonate of ammonia. The phosphoric acid and fluorine are then precipitated by a lime salt, the carbonate of lime removed from the precipitate in the manner above directed, and after the weight of the phosphate of lime and fluoride of calcium together has been determined, the whole of the precipitate is treated in a large platinum crucible with concentrated sulphuric acid at a very gentle heat, until a piece of glass laid over the crucible is no longer etched. The residue in the crucible is then treated with alcohol, which removes the phosphoric and the excess of sulphuric acid, but leaves undissolved the sulphate of lime, the weight of which is determined. After adding water to the alcoholic solution, the alcohol is expelled at a gentle heat, and the phosphoric acid then thrown down as ammonio-phosphate of magnesia. From the loss in weight found on comparing the combined weight of the phosphoric acid and of the lime with that of the original precipitate, the amount of fluorine in it can be calculated; for it is to this loss in weight, as the equivalent of fluorine is to the equivalent of fluorine less the atomic weight of oxygen.

In solutions which contain an alkaline fluoride and alkaline phosphates, the phosphoric acid can be separated from the fluorine by a solution of basic protonitrate of mercury. The latter yields, it is true, with a solution of an alkaline fluoride, a copious yellowish precipitate, which is insoluble in the solution of the fluoride, but soluble in an excess of the solution of the protoxide of mercury; only the phosphoric acid, therefore, is precipitated by the latter. After drying the precipitate, it is mixed with carbonate of soda, and in order to determine the amount of phosphoric acid present, treated as described in the author's former paper.

The separation of sulphates from fluorides is difficult. Heavy spar and fluor spar occur mixed in nature; but in this mixture it is impossible to effect a separation by treatment with muriatic or nitric acid, as would be expected. If the undissolved sulphate of baryta, after treatment with these acids, is washed with water, it contains some fluoride of barium, and also some sulphate of lime if the washing with water has not been continued sufficiently long. A similar decomposition takes place in a mixture of sulphate of baryta and fluoride of calcium on the action of muriatic acid, as occurs with a mixture of sulphate of baryta and chloride of calcium at a red heat, the fluoride of barium dissolved in the acid is reconverted by the simultaneously-dissolved sulphate of lime into sulphate of baryta. But if the insoluble precipitate is not washed with pure water, but with dilute muriatic acid, it may be brought to such a pitch that it contains no more fluoride of barium, which is at length dissolved by the acid; but then the sulphate of lime is difficult to remove from, so that the determination of the sulphate of baryta is always rendered inaccurate.

As the separation of sulphate of baryta from fluoride of calcium cannot be effected in the moist way by treatment with muriatic acid, the mixture should be decomposed by fusion with carbonated alkali and the addition of silicic acid. When the fused mass is cold, it is treated with water, the silica in solution precipitated by carbonate of ammonia, the alkaline liquid is supersaturated with muriatic acid and precipitated with chloride of barium. The correct amount of sulphate of baryta is obtained, which is also free from fluoride of barium. —*Bericht der Berlin. Acad.*, Dec. 1849, p. 357.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

March 4, 1850. (Robert Porrett, Esq., Treasurer, in the Chair.)

Mr. Warington laid before the Society a detail of some experiments which he has been conducting for the last twelve months, on the preservation of fish in a limited and confined portion of water, through the medium of the growth of aquatic plants, thus sustaining the balance between the animal and vegetable kingdom in that fluid, by which they are made mutually to subserve each for the other's nutriment, and even for its indispensable wants and vital existence, and illustrating in a marked degree that wonderful and beautiful provision which is seen so amply displayed throughout the whole circle of organized life.

THE CHEMICAL GAZETTE.

No. CLXXX.—April 15, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of some Alkaloids. By T. Wertheim.

1. When narcotine is treated at a temperature of 428° with an excess of hydrate of potash or soda, a colourless distillate, of a penetrating ammoniacal odour and pungent taste, is obtained. Its vapour turns red litmus-paper blue, and forms a white cloud with muriatic acid. The distillate owes these properties to the presence of an exceedingly volatile liquid base, of which it constitutes a concentrated aqueous solution. When diluted with much water, it has, besides the ammoniacal odour, a peculiar smell of Dutch herrings; the taste of the dilute solution is slightly bitter. With muriatic and sulphuric acids this base forms salts, which are readily soluble in water and alcohol. From the concentrated alcoholic solution of the muriate, the platinum double salt is thrown down by the chloride of platinum as an amorphous pale yellow precipitate. From the hot aqueous solution it separates in remarkably fine patches of crystals of a pale orange-red colour. When heated to 212°, the perfectly pure double platinum salt exhibits in a slight degree the above-mentioned smell of herring, without however being perceptibly altered. Several accordant analyses gave for it the formula $C^6 H^9 N + ClH + PtCl^2$, whence immediately results for the base itself the expression $C^6 H^9 N$. A glance at this formula and the above-described properties of this base immediately indicates that it belongs to the series of the bases recently discovered by A. Wurtz, in which it represents that member corresponding to the hypothetical æther $C^6 H^7 O$. The new base must therefore be regarded as $C^6 H^7, NH^2$, or as $C^6 H^6, NH^3$. Since Wurtz has derived the names of his bases from the nomenclature of the corresponding alcohol series, it appears desirable to form the name for this base in an analogous manner. If we were to select, for instance, the name œnyle for the alcohol radical $C^6 H^7$, which Berzelius proposed for Kane's mesityle, the new base would receive the name œnylamine or œnylia, which would certainly be shorter and more euphonious than the names metacetamine or metacetia, which might be derived from the metacetonic acid.

The next question which arises is, how this base has originated from the atom of the narcotine. If we were to presume it to exist in it, then we should have for narcotine the expression $(C^6 H^9 N + C^{40} H^{16} O^{14})$ or $(C^6 H^9 N + 2[C^{20} H^8 O^7])$. The group $C^{20} H^8 O^7$

differs however from the complex one of opianic acid merely by 2 equivs. oxygen less; so that according to this splitting, narcotine might be conceived as a combination of 1 equiv. œnylamine with 2 equivs. of an acid, which might be called opianous acid. But plausible as this view might be of itself, cotarnine obtained by Wöhler and Blythe is evidently a more proximate product of decomposition of narcotine than the œnylamine, and we are therefore more justified in assuming that the cotarnine is originally contained in the atom of the narcotine, and that the œnylamine is formed from the cotarnine by a second splitting. If we admit with Wöhler 26 equivs. carbon in cotarnine, there likewise remains, after deducting the œnylamine, a group from which by simple oxidation opianic acid may be formed. It is probable, therefore, that after satisfactorily establishing the formula for cotarnine, a correct view of both modes of decomposition will follow without great difficulty. I intend making some direct experiments with cotarnine in this direction.

2. When morphine is treated, at a temperature of 392° F., with an excess of hydrate of potash, a distillate is obtained, the external characters of which differ but slightly from those above described. The odour is equally penetrating and ammoniacal, the taste acrid and pungent. The sulphuric compound of the base is but very sparingly soluble in alcohol; the muriate is very readily soluble in alcohol and water. From the alcoholic solution of the muriate, chloride of platinum throws down a double salt of a pale yellow colour. In water it is readily soluble, especially on the application of heat, and separates from the hot solution on cooling in beautiful golden scales. The composition of this double salt is $C^2 H^5 N + ClH + PtCl^2$; the base obtains the formula $C^2 H^5 N$, *i. e.* the formula of methylamine. Further experiments, in which I am at present engaged, will, I hope, furnish the desired explanation respecting the production of this base from morphine.

3. As is well known, quinoline is obtained by the action of hydrate of potash in a state of fusion upon quinine. If in this operation too high a temperature is avoided, the residue of the distillation will be found to contain a larger or smaller amount of formiate of potash. A temperature of 356°–374° suffices to effect this decomposition. In order to explain the action which occurred in this operation, it appeared above all requisite to submit the formula of quinine to a careful examination. For this purpose the combination of this base with hydrosulphocyanic acid was prepared; it was obtained in beautiful light lemon-coloured crystals of the hemiorthotype system, of such size and regularity that they could be accurately measured with the reflecting goniometer. The analyses of this compound, which agreed very well with each other and also with the calculated result, gave the formula $C^{20} H^{12} NO^2 + C^2 NS^2 H$, whence follows for quinine the expression $C^{20} H^{12} NO^2$, consequently the same formula which Liebig advanced for it some years ago, but which has since been much controverted by Laurent and other chemists. For still greater certainty, several other beautiful crystalline compounds of quinine were prepared and analysed; their examina-

tion led to the same result for the composition of quinine. The compounds examined were,—1st, a double compound of hydrocyanate of quinine with protocyanide of platinum $= \dot{Chi}\,CyH + PtCy + 1aq$; 2nd, a double compound of hydrochlorate of quinine with percyanide of platinum $= \dot{Chi}\,ClH + PtCy^2$; 3rd, a double compound of hydrosulphocyanate of quinine with percyanide of mercury $= 2(\dot{Chi}\,CyS^2H) + HgCy$; and lastly, a similar compound of hydrosulphocyanate of quinine with perchloride of mercury $= 3(\dot{Chi}\,CyS^2H)\,4(HgCl)$. The hydrosulphocyanate of quinine and the double compounds 1 and 2 were prepared by precipitating the solution of sulphate of quinine with solutions of the corresponding potash salts. The double compounds 3 and 4 were obtained by precipitating the solution of sulphocyanide of quinine with solutions of percyanide and perchloride of mercury.

Now if we subtract from this formula of quinine that for quinoline, $C^{18}H^8N$, it leaves the expression $C^2H^4O^2$. From this group, which is isomeric or identical with the hydrate of the oxide of methyle, the formic acid obtained by the action of hydrate of potash has evidently originated. We should therefore perhaps be justified, from what has been above stated, in regarding quinine as a conjugate compound of quinoline with the hydrate of the oxide of methyle or some isomeric group. But another view however might be hazarded, and which must obtain a high degree of probability from the very important discoveries of Wurtz. Instead of $C^2H^4O^2 + C^{18}H^5N$, we may also write $(C^2H^2 + C^{18}H^5N + 2aq)$, and quinine would then have to be regarded as methylia in which ammonia is replaced by quinoline. I reserve this subject also for future investigation, and shall then communicate the analyses to which I have referred in the preceding notices.—Liebig's *Annalen*, Feb. 1850.

On the Action of Ammonia upon the Product of Oxidation of Xanthates by Iodine. *By* H. Debus.

Among the products of the metamorphosis of xanthic acid, that produced by the action of iodine is remarkable from its stability. It can, moreover, be easily obtained in quantity. This circumstance has induced the author to make this series of bodies the subject of more accurate investigation. For the preparation of this product the xanthate of lead was selected, which, according to the author, is easily obtained in the following manner:—

Xanthate of Lead, $C^6H^5OS^4, PbO$.—Hydrate of potash is dissolved in alcohol of 0·833, sulphuret of carbon and hydrated oxide of lead added, and the mixture set aside for six to eight hours, agitating it frequently. Sulphuret of lead and large colourless crystals of xanthate of lead are obtained; another portion of oxide of lead is held in solution by the potash. It is filtered, and the clear liquid

diluted with water as long as a milky turbidness results. The liquid soon afterwards clears, with separation of the xanthate of lead, in long colourless needles. The mother-liquor from this lead salt furnishes on evaporation a mixture of sulphuret of potassium, dithionite, carbonate and sulphocarbonate of potash.

The xanthate of lead is insoluble in cold water, alcohol and æther. Boiling water decomposes it, with separation of sulphuret of lead, sulphuret of ethyle, and probably of dithionous acid. Dilute nitric acid converts this compound, after several hours, into a kind of fatty body; by longer contact, or when a concentrated acid is used, into a yellow oil and sulphate of lead. Acetic acid does not alter the xanthate of lead even at 212°; hydrochloric and sulphuric acids appear to decompose it at the ordinary temperature; potash dissolves it, with separation of sulphuret of lead. Chromic acid converts the salt on boiling into a brown powder; protochloride of tin separates chloride of lead, with formation of some products which were not further examined. When sulphuret of potassium is heated with it, sulphuret of lead and xanthate of potash are formed. Sulphuretted hydrogen does not blacken it.

The salt is decomposed at 252° F.; and at 284° a yellow oil, having the odour of impure cyanide of ethyle, distils over. Half the weight of the salt employed is left as sulphuret of lead in the retort. On rectification, the boiling-point of the distillate rises from 122° to 572°. This substance could not be purified by heating with sulphuric acid, in which operation sulphurous acid was disengaged, and the mass became black, or by distillation with solution of caustic potash, according to Couerbe's statement. The impure substance does not solidify at 14° F.; it is heavier than water, and burns with a blue flame and disengagement of sulphurous acid. It is insoluble in water, but soluble in every proportion in alcohol. The solutions are neutral, and are not precipitated by nitrate of silver, sulphate of copper, acetate of lead and chloride of calcium, but they furnish a white precipitate with perchloride of mercury. The latter precipitate consists for the greater part of protochloride of mercury. The salt used for analysis was dried *in vacuo*, and gave—

Carbon.....	16·48	15·75	6	= 36·0	16·01
Hydrogen.....	2·56	2·27	5	5·0	2·22
Oxygen.....	..	..	2	16·0	7·11
Sulphur.....	29·15	..	4	64·0	28·49
Lead.....	45·78	..	1	103·8	46·17

Binoxysulphocarbonate of Ethyle, $C^6 H^5 O^2 S^4$.—Iodine is allowed to act upon a solution of the xanthate of lead in alcohol by adding it in small portions until the resulting brown colour no longer disappears. The liquid is filtered from iodide of lead, and diluted with its weight of water, and the mixture set aside for ten or twelve hours at a temperature of about 54° F. Binoxysulphocarbonate of ethyle is then obtained in minute white prismatic crystals, contaminated with iodide of lead, from which it is freed by recrystallization.

When the binoxysulphocarbonate of ethyle is prepared from xanthate of potash, the alcoholic liquid may be diluted with water immediately after its treatment with iodine: the binoxysulphocarbonate crystallizes out, and the iodide of potassium remains in solution. If a concentrated solution of the xanthate in alcohol has been employed, the product separates, on diluting its solution with water, in the form of a yellow oil, which in the course of several hours changes into crystals. From dilute solutions it is obtained in concentric groups of longish white prisms. They have a pungent taste, and melt at 82° to a yellowish oil of a peculiar odour, which is several hours before it again solidifies. When heated to 212°–248°, the binoxysulphocarbonate of ethyle is apparently not altered in its other properties, but it now no longer crystallizes on cooling. Its formation may be expressed by the following equation—

$$C^4 H^5 O, 2CS^2, MO + I = C^4 H^5 O, C^2 S^4 O + MI,$$

and its decomposition at a high temperature by—

$$2(C^4 H^5 O, C^2 S^4 O) = 2(C^4 H^5 O, CS^2) + CS^2 + CO^2 + S^2,$$

as already stated by Desains.

Æther and anhydrous alcohol dissolve this substance very readily, hydrous alcohol less so. The solutions are not precipitated by acetate of lead, nitrate of silver, nor most of the salts of the metallic oxides; on boiling the solution mixed with nitrate of silver, sulphuret of silver is precipitated. Perchloride of mercury throws down a white precipitate, which turns black at 104°; and chloride of platinum, after some time, a fine, pulverulent brown precipitate. Peroxide of mercury, oxide of lead, peroxide of lead, sulphurous acid, sulphuretted hydrogen and hydrochloric acid appear not to act upon it. Sulphuric acid dissolves the binoxysulphocarbonate of ethyle with a slight disengagement of sulphurous acid; nitric acid with formation of nitric oxide, sulphuric acid and a peculiar acid not further examined. Dissolved with potash and alcohol, sulphur separates, and a salt is found in the liquid which has the crystalline form and the reactions of the xanthate of potash. The analysis of the binoxysulphocarbonate of ethyle gave the following results, agreeing with those of Desain:—

	Debus.		Desains.				
	I.	II.	III.	IV.			
Carbon	29·75	29·80	29·4	29·2	6	= 36	29·75
Hydrogen	4·18	4·27	4·2	4·3	5	5	4·13
Oxygen	..	..	..	..	2	16	13·22
Sulphur	..	53·50	53·4	53·0	4	64	52·89

Ammonia and Binoxysulphocarbonate of Ethyle.—When a current of dry gaseous ammonia is passed into an alcoholic solution of the binoxysulphocarbonate of ethyle until no more sulphur separates, and it is then filtered and the liquid evaporated to dryness, crystals of the xanthate of the oxide of ammonium are obtained, which are permeated by a new oily substance, xanthamide. They can be separated by æther, which dissolves the latter. Xanthamide has

the composition $C^6 H^7 O^2 S^2 N$; consequently 2 atoms of binoxysulphocarbonate of ethyle absorb 2 atoms of ammonia, and separate into 1 atom of xanthate of the oxide of ammonium, 2 atoms of sulphur and 1 atom of xanthamide, as follows:—

$$2[(C^4 H^5 O, C^2 S^4 O) + NH^3] = C^4 H^5 O, 2CS^2, NH^4 O + S^2 + C^4 H^5 O^2, C^2 S^2 NH^2.$$

Xanthate of the Oxide of Ammonium, $C^4 H^5 O, C^2 S^4, NH^4 O$.—When the aqueous solution of this salt, prepared as above described, is allowed to evaporate spontaneously in the air, the greater portion separates in shining crystals, resembling urea, whilst a small portion is decomposed into sulphuret and sulphocyanide of ammonium. In the water-bath the salt evaporates entirely with the aqueous vapour; *in vacuo* it can be obtained in a solid form without decomposition. On ebullition for a short time with ammonia, it seems to experience no change; but after a longer time, sulphocyanide of ammonium is formed by the presence of ammonia. It is decomposed on long boiling with sulphuret of ammonium. Heated in a tube, it forms a white sublimate, sulphuret of ammonium, a yellow oily body, and apparently sulphocarbonate of ammonium, and leaves a slight black residue. Acids separate xanthic acid as a pale yellow-coloured oil. It gives the same reactions with metallic solutions as the xanthate of potash. Whether preserved dry or not, the xanthate of the oxide of ammonium parts with ammonia, and is decomposed. Analysis gave 27·00 per cent. carbon and 6·83 hydrogen. Its solution furnished the above-described lead salt on precipitation with a slightly acid solution of acetate of lead.

Xanthamide, $C^6 H^7 O^2 S^2 N$, that is $C^4 H^5 O + CNH^2 O + CS^2$ or $C^4 H^5, CNH^2 O, CO^2 + C^4 H^5 S, CNH^2 S, CS^2$.—This substance contains 2 atoms of sulphuretted hydrogen less than the xanthate of ammonia. As above stated, it is obtained at first as an oil; but on evaporation of the æther, by means of which it has been separated from the xanthate of ammonia, it crystallizes. By dissolving it in as little alcohol as possible, and slow evaporation of the latter in the air, the compound is obtained in perfectly pure large crystals. Xanthamide may also be prepared by evaporating in the water-bath the alcoholic solution of the binoxysulphocarbonate of ethyle, which has been merely treated with ammonia. It forms the residue; any adherent xanthate of ammonia can be readily removed by a little water.

Xanthamide is also formed when ammonia is poured over binoxysulphocarbonate of ethyle, and left for several days in the cold, or five to six hours between 140° and 158°; sulphur is eliminated. The solution, which is coloured of a dark yellowish-brown by polysulphuret of ammonium, contains along with xanthamide xanthate of the oxide of ammonium; or, when the mixture has been digested for some time with an excess of ammonia, the products of decomposition of the latter. On separating the sulphur by filtration, and evaporating the liquid in the water-bath so as to remove all sulphuret of ammonium, xanthamide first crystallizes from the residual liquid on spontaneous evaporation; and subsequently, if the evaporation

be assisted by heat, sulphocyanide of ammonium, resulting from the decomposition of the xanthate of ammonia.

When dry binoxysulphocarbonate of ethyle is acted upon by dry ammoniacal gas at a temperature of about 158°, it is decomposed in the same manner. The volatile products formed perfectly agree with the products of decomposition of the xanthate of the oxide of ammonium obtained under similar conditions, whilst that substance itself could not be detected. We find sulphuret of carbon, sulphocarbonate of ammonium, sulphocyanide and sulphuret of ammonium; further, as less volatile products of the decomposition, xanthamide, sulphur and sulphocyanide of ammonium.

Xanthamide forms truncated, four-sided, rhombic pyramids, belonging to the monoclinic system. It is rather difficult of solution in water, but dissolves in every proportion in alcohol and æther. The solutions are neutral, and are not precipitated by nitrate of silver, acetate of lead, sulphate of copper and salts of baryta, but they are by chloride of platinum and perchloride of mercury. Oxide of mercury, oxide of silver, oxide of lead and carbonate of silver decompose the substance, with formation of a sulphuret of the metal, and of a substance which irritates the eyes very powerfully, and the odour of which resembles acroleine. When the decomposition is complete and the filtrate from the sulphuret is distilled, a small quantity of a neutral substance passes over along with the solvent of the xanthamide, from which it was impossible to separate it. The residue in the retort furnished, on evaporation in the water-bath, a quantity of a salt of ammonia, small in proportion to the xanthamide employed, the acid in which gave no precipitate with any reagent, and developed the odour of cyanic acid after its separation by sulphuric acid.

Xanthamide dissolves readily in concentrated sulphuric acid. On diluting the acid with water, it is again precipitated unaltered; but if the acid solution is set aside for several days or gently heated, it disengages a large amount of sulphurous acid, without any blackening, after removal of which and of the sulphuric acid with carbonate of baryta, a non-crystalline baryta salt is obtained of an acid, which is not precipitated by salts of silver, lead, copper, mercury and lime. Nitric acid converts xanthamide into sulphuric acid and an acid which has not been further examined. Caustic potash and barytic water decompose it immediately on boiling into alcohol and hydrosulphocyanic acid; ammonia resolves it at 302° into carbonic acid, hydrosulphocyanic acid, and some compounds having a disagreeable odour, resembling mercaptan. The analysis of xanthamide, dried *in vacuo* over sulphuric acid, furnished—

Carbon	34·28	34·62	34·19	6	36	34·33
Hydrogen	6·72	6·72	6·67	7	7	6·66
Oxygen	..	..	..	2	16	15·23
Sulphur	32·28	32·43	31·31	2	32	30·47
Nitrogen	12·90	..	..	1	14	13·36

Xanthamide-perchloride of Platinum with Xanthamide-protochloride of Platinum, $PtCl^2$, C^4H^5O; $C^2S^2ONH + PtCl$, C^4H^5O;

C^2S^2ONH.—On the addition of perchloride of platinum to a spirituous solution of xanthamide, a yellow crystalline precipitate first separates, and then for several days crystalline laminæ. The latter are probably contaminated with sulphuret of platinum. The highly-coloured mother-liquor from these precipitates disengages muriatic acid vapours on evaporation, with separation of a brown oil, which is gradually volatilized with the alcoholic and aqueous vapours. The residue is a dark-coloured substance, which appears to be sulphuret of platinum and chloride of ammonium.

This substance is insoluble in water, alcohol and æther; potash, nitric and muriatic acids, have no action upon it; concentrated sulphuric acid acts upon it only with the assistance of heat; aqua regia dissolves it. At 248° F. it is decomposed. The yellow crystalline precipitate, dried over sulphuric acid, gave—

Carbon	13·97	13·39	..	12 =	72·0	14·01
Hydrogen	2·69	2·72	..	14	14·0	2·72
Oxygen	..	..	..	4	32·0	6·24
Sulphur	..	13·35	..	4	64·0	12·46
Nitrogen	..	..	..	2	28·0	5·45
Platinum	38·04	38·26	37·85	2	197·4	38·43
Chlorine	19·08	23·30	..	3	106·2	20·69

Decomposition of Xanthamide by Hydrate of Baryta.—On boiling xanthamide with hydrate of baryta, it furnishes ammonia and alcohol, sulphocyanide of barium being left in the retort:—

Alcohol	$C^4H^6O^2$
Hydrosulphocyanic acid	$C^2H \quad S^2N$
Xanthamide	$C^6H^7O^2S^2N$.

Distillation of Xanthamide. Products: Mercaptan and Cyanuric Acid.—Xanthamide melts on the application of heat; at 212° it disengages a little gas; at 347° it boils, and a liquid of a disagreeable odour passes over. The distillation is carried on at 305°; the distillate smelt of mercaptan and cyanic acid; it was rectified over chloride of calcium; the boiling-point rose from 122° to 446°. The first portions which passed over were colourless, the last were yellow; both had a faint alkaline, almost neutral reaction, and when dissolved in alcohol, furnished, with silver, copper and lead salts, white precipitates; with perchloride of mercury, a very copious precipitate, which became subsequently converted into crystalline laminæ. This mercurial compound is the

Mercaptide-mercury-perchloride of Mercury, $C^4H^5S, HgS + HgCl$.—It is sparingly soluble in alcohol, æther and water; from a boiling saturated alcoholic solution it separates in white laminæ. It is but slightly acted upon by nitric acid. Evaporated to dryness with a solution of caustic potash, a small portion is decomposed with elimination of peroxide of mercury. Sulphuret of ammonium first colours it black, and then red, with formation of vermilion. Heated in a tube to 320°, no change is perceived; but at a somewhat higher temperature the compound acquires a yellowish colour, and a yellow

ætherial liquid is volatilized, after the escape of which the residue again becomes white, but at a still higher temperature black, and furnishes a white and black sublimate. It gave on analysis—

Carbon	8·39	8·83	4 =	24·0	8·10
Hydrogen	1·73	1·64	5	5·0	1·69
Sulphur	..	12·08	2	32·0	10·89
Mercury.....	66·74	..	2	200·0	67·74
Chlorine.....	..	11·90	1	35·4	11·85

Cyanuric Acid is left as a grayish-white mass in the distillation of xanthamide; after being purified by recrystallization, it exhibited all the properties of cyanuric acid, and yielded—

Carbon.....	28·40	28·02	2 =	12	27·83
Hydrogen	2·50	2·59	1	1	2·31
Oxygen	36·41	36·70	2	16	37·05
Nitrogen	32·69	32·69	1	14	32·81

Tribasic Cyanurate of Silver, $C^6\,H\,N^3\,O^4, 3AgO$, was obtained by mixing a dilute hot solution of the acid with nitrate of silver, and adding dilute ammonia to the clear liquid so long as a precipitate was formed. This salt was insoluble in water and alcohol, sparingly soluble in acetic acid, but readily in nitric acid; potash had no action upon it in the cold; on the application of heat, it eliminated oxide of silver. The compound, dried between 194° and 230°, gave—

Carbon	7·60	7·40	6 =	36	7·85
Hydrogen	0·30	0·30	1	1	0·21
Oxygen	..	..	7	56	
Nitrogen	8·98	..	3	42	9·10
Sulphur.....	70·25	70·41	3	324	70·57

Xanthamide therefore is decomposed into mercaptan and cyanuric acid, $C^4\,H^6\,S^2 + C^2\,HNO^2 = C^6\,H^7\,S^2\,NO^2$.—Liebig's *Annalen*, lxxii. p. 1.

Further Observations on the Atomic Weight of Mannite. *By* Dr. W. Knop.

In a former paper I have dwelt upon the necessity of our possessing an accurate analysis of nitromannite, in order to determine the atomic weight of mannite. The January number of the 'Annalen der Chemie und Pharmacie' contains a paper on the composition of this substance by Strecker. With respect to the preparation and properties of nitromannite, as described by the author, they agree with what has been stated at page 85, to which we may therefore refer. The following however are the results of that chemist's analysis. Nitromannite, twice recrystallized from alcohol, and dried over sulphuric acid, furnished—

	Strecker.			
Carbon.....	16·07	6 =	36	15·93
Hydrogen.....	1·94	4	4	1·77
Nitrogen	18·20	3	42	18·58
Oxygen.....	63·70	18	144	63·72

The formation of nitromannite takes place in the following manner:—$C^6 H^7 O^6 + 3NO^5 H = C^6 H^4 N^3 O^{18} + 3HO$. These numbers evidently decide for the formula $C^6 H^7 O^6$.

Strecker has also examined the analytical results obtained by Flores Domonte and Ménard on the one hand, and by Svanberg and Staaf on the other. These results, which do not agree with each other, are compared in the following table with the superscribed formulæ:—

	Domonte and Ménard.		Svanberg and Staaf.		$C^{12} H^9 N^4 O^{29}$.	$C^{12} H^7 N^5 O^{32}$.
Carbon....	17·3	17·1	19·8	19·0	19·5	17·8
Hydrogen	1·8	1·9	2·1	2·2	2·4	1·7
Nitrogen ..	17·5	17·0	..	..	15·2	17·3
Oxygen ..	..	..	..	..	62·9	63·2

The result of Strecker's comparison of his analyses with those last mentioned is, that the latter numbers vouch little for the probability of their accuracy; and Strecker's results, according to which nitromannite absorbs 6 atoms of nitric acid for every 12 atoms of carbon, and not 5 or 4, deserve the preference. He moreover shows, by repetition of the analysis of mannite and a comparison of the results previously obtained, that the formula of mannite is most probably $C^6 H^7 O^6$, or $C^{12} H^{14} O^{12}$.

The chief result of the preceding investigation agrees consequently with what I formerly stated respecting the formula for mannite. As regards the constitution of nitromannite, I may observe, that in my opinion it is extremely probable that the nitric acid is contained in it as such, and not as hyponitric acid. When, for instance, nitromannite is dissolved in concentrated sulphuric acid, it is soon decomposed without any evolution of gas; the solution remains perfectly colourless, and on diluting the acid with water, there is no longer a precipitate formed. When the sulphuric solution is poured into much water, very little red vapour is perceptible; but this is the case when it has been kept for any length of time, or been heated, and so hyponitric acid been produced. I have also applied Zinin's test to nitromannite. On treatment with sulphuret of ammonium, a violent reaction ensues; but I could not detect a trace of any nitrogenous mannitic substance, but the sulphuretted hydrogen appeared rather to have a reducing action like the metals. In this respect, therefore, nitromannite also differs from the substances containing hyponitric acid.

I will now pass in review the existing data for fixing the formula of mannite. The supposed *lead compounds of mannite* of Favre do not exist in my opinion. On repeating his experiments, and in my examination of the combinations of mannite, I have never obtained crystalline bodies. They are most probably mixtures of basic lead salts with uncombined mannite.

The *sulphomannitic acid* of Favre and its lead salt, $4PbO, 2SO^3 + C^6 H^5 O^4$, are not at all likely to be chemical compounds having the above composition; for the circumstances under which they are

obtained are such that the sulphomannitic acid is kept in solution for some length of time, while I have proved by several experiments that the acid is slowly decomposed under these circumstances.

From the above considerations and the results enumerated in my former paper, I am led to consider as erroneous the statements of Favre, that mannite, on entering into combination, parts with 2 atoms of water, $C^6 H^7 O^6$, becoming $C^6 H^5 O^4$.

The formula of mannite, $C^8 H^9 O^8$, proposed by Schnedermann and myself, is founded solely on the fact, that analyses of the sulphomannitates furnished for 4 equivs. carbon 2 equivs. sulphur and 1 atom of base; and a conjunct capable of taking up 6 atoms of sulphuric acid appeared at that time too unusual. These assumptions, which necessarily demanded further investigation, may now be combined in the following manner. Since the simplest relations for

1. Mannite..... $= C^6 H^7 O^6$, Liebig,
2. Nitromannite..... $C^6 H^4 O^3 (NO^5)^3$, Strecker,
3. Formiate of mannite . $C^6 H^7 O^6, C^2 H O^3$, Knop,
4. Sulphomannitates.... $C^4 : S^2 : RO$, Knop and Schnedermann,

the formula which combines all these relations appears to have the form of $C^{12} H^{14} O^{12}$, according to which

Nitromannite ..... $= C^{12} H^8 O^6 (NO^5)^6$.
Sulphomannitic acid.. $C^{12} H^8 O^6 (SO^3)^6 + 3HO + 3HO$.
Sulphomannitates.... $C^{12} H^8 O^6 (SO^3)^6 + 3HO + 3RO$.
Formiate of mannite.. $C^{12} H^8 O^6 (2C^2 HO^3 + 4HO)$.
Mannite..... $C^{12} H^8 O^6 (HO)^6$.

As regards the explosive properties of nitromannite, it results from Strecker's analyses, and from the composition $C^{12} H^8 N^6 O^{36}$, that the oxygen suffices to burn completely the whole of the hydrogen and carbon. The phænomena of the reduction of nitromannite by metals may be equally well explained. When, for instance, nitromannite, dissolved in weak alcohol, is treated with iron, the chief products formed may be represented as follows:—

$$C^{12} H^8 N^6 O^{36} + HO = 12CO^2 + 3NH^3 + 3NO^2 + O^7.$$

There are however some other products formed in this reaction, as the alcohol has no longer an alkaline, but a slightly acid reaction; probably volatile fatty acids are formed from the alcohol by the excess of oxygen which the nitromannite contains. In the treatment with muriatic acid and excess of iron, the following decomposition probably occurs:—

$$C^{12} H^8 N^6 O^{36} + HCl = 12CO^2 + 3NH^3 + 3NO^2 + O^6 Cl.$$

In the presence of metals and an excess of acid, the last member is naturally converted into water and a chloride of the metal.—*Pharm. Cent. Blatt.*, Jan. 23, 1850.

Observations on Cholestrophane. *By* Prof. Rochleder.

When cholestrophane is boiled with potash, it disengages an ammoniacal odour, as already observed by Dr. Stenhouse; carbonate of potash is formed, and there likewise remains in combination with the potash an acid, which, after saturating the solution with nitric acid, is precipitated by nitrate of silver as a heavy white powder. This silver salt has all the properties of the oxalate of silver; it explodes gently when heated. To obtain perfect certainty on this point, the salt was analysed; the results gave accurately the composition of the oxalate of silver. Cholestrophane furnishes, besides oxalic acid, *carbonic acid*, and disengages *ammoniacal vapours* precisely like a compound of urea. This behaviour and the formation of oxalic acid, together with the composition of cholestrophane and its origin by oxidation from amalic acid, show that it should be regarded as a conjugate parabanic acid:—

Cholestrophane $= C^{10} H^6 N^2 O^6 = C^4 H^4 + \underbrace{C^6 N^2 O^4 + 2HO}_{\text{Parabanic acid.}}$,

or $C^6 N^2 \left.\begin{matrix} H \\ C^4 H^3 \end{matrix}\right\} O^6$.

Amalic acid $= C^{12} H^7 N^3 O^8 = C^4 H^4 + \underbrace{C^8 H^3 N^2 O^8}_{\text{Alloxantine, anhydrous.}}$,

or $= C^8 \left.\begin{matrix} H^2 \\ C^4 H^3 \end{matrix}\right\} N^2 O^8$.

Accordingly alloxantine ..... $= C^8 H^3 N^2 O^8 + 2HO$.
Alloxan would then be ..... $= C^8 H^3 N^2 O^9 + HO$.
Caffeine $C^{16} H^{10} N^4 O^4$ ..... $= C^2 N + C^2 H^5 N + [C^4 H^4 + C^8 HN^2 O^4]$.

It contains therefore a group, $C^4 H^4 + C^8 H N^2 O^4$, *i. e.* uryle, which in uric acid is combined with urea; in the present case it is united with 1 equiv. hydrogen, or, what amounts to the same, it is urylous acid, $C^8 H N^2 O^4 = C^8 N^2 O^3 + HO$, whilst urylic acid $= C^8 N^2 O^4$.

The product resembling murexide, which is formed by the action of ammonia upon amalic acid, must be analogous to murexide, *i. e.* a conjugate murexide compound. The alloxantine of amalic acid must furnish murexide, which is conjoined with $C^4 H^4$. Murexide is formed from 3 equivs. of alloxan and alloxantine $= C^{24} H^{12} N^{10} O^{16}$. When the 3 equivs. of alloxantine (anhydrous) of the amalic acid are converted into $C^{24} H^{12} N^{10} O^{16}$, $3C^4 H^4$ must remain conjoined. With this agree the analyses I have made, which will be communicated in detail as soon as I have examined some other products.

Thus it is, for instance, very probable that cholestrophane, on ebullition with potash, does not disengage ammonia, but ammonia $+ C^4 H^4 = C^4 H^7 N$, *i. e.* the ethylamine of Wurtz.

This series of products exhibits an interesting connexion with those which Liebig and Wöhler obtained in their investigation on uric acid.—Liebig's *Annalen* for January 1850.

On a Product of Decomposition of Tyrosine. By Dr. A. Strecker.

When ordinary nitric acid is poured over tyrosine, it quickly dissolves with a yellow colour, and after a few minutes red vapours are disengaged, whilst at the same time a yellow crystalline powder separates. The solution on evaporation furnishes crystals of pure oxalic acid. When the nitric acid is boiled with the tyrosine, no yellow powder is obtained, but only oxalic acid, on evaporation. As De la Rue obtained, in the treatment of his tyrosine from cochineal with nitric acid, long acicular crystals, which he states are probably a new acid, I will observe that I have assured myself of the identity of the acid obtained by me with oxalic acid by its appearance, its behaviour when heated in a tube, and its reaction with salts of lime.

When however tyrosine is mixed with water, and nitric acid added in drops, it soon dissolves, and a further addition of nitric acid causes a yellow colour without any evolution of gas. If we discontinue the addition of nitric acid as soon as the liquid has become yellow, and leave it undisturbed, a yellow powder, resembling that above mentioned, separates in the course of several hours, but more quickly if the sides of the glass are rubbed with a glass rod. The liquid filtered from the powder leaves scarcely a residue on evaporation. The yellow crystalline powder is sparingly soluble in cold, more readily in boiling water, and crystallizes on cooling in small laminæ, which usually possess a brown, almost bronze colour, but when powdered exhibit a yellow colour. They dissolve also in cold alcohol, more readily in hot, but less than in water. The solutions have an acid reaction, a yellowish colour and a bitter taste. This substance dissolves easily in ammonia and in potash with an intense red colour. The substance for analysis was dried over sulphuric acid, and burnt with chromate of lead. It furnished—

Carbon.....	37·54	37·56	18 =	108	37·37
Hydrogen	4·04	4·06	11	11	3·81
Nitrogen	14·37	..	3	42	14·53
Oxygen	..	..	16	128	44·29

If we compare this formula with that found by Hinterberger for tyrosine, $C^{18}H^{11}NO^6$, it will be observed that the elements of 2 equivs. of anhydrous nitric acid have entered:—

$$C^{18}H^{11}NO^6 + 2NO^5 = C^{18}H^{11}N^3O^{16}.$$

Such a mode of decomposition by nitric acid would stand quite isolated. However, the formula $C^{18}H^{11}N^3O^{16}$ may be split in such a manner that it represents the nitrate of a nitro-compound of tyrosine, $C^{18}H^{11}N^3O^{16} = C^{18}\left.\begin{matrix}H^{10}\\NO^4\end{matrix}\right\}NO^6 + NO^6H$. This view of the constitution of this body, which I consequently name nitrate of nitro-tyrosine, is confirmed by experiment. If it be dissolved in water, a crystal of the protosulphate of iron added, and then sulphuric acid, the reaction of nitric acid is obtained. Further, the hydrate of nitric acid may be expelled by sulphuric acid, and the crystals obtained on evaporation contain sulphuric acid in its place. This

view obtains further confirmation from the following analyses of the silver compound.

Nitrotyrosine and Oxide of Silver.—When the nitrate of nitrotyrosine is dissolved in dilute ammonia, and nitrate of silver added, a yellow amorphous precipitate is formed in the cold, which on ebullition acquires a bright red, or in the presence of ammonia a dirty brown colour. The precipitate is soluble both in ammonia and in nitric acid. It explodes slightly when heated. The pure yellow silver compound was dried over sulphuric acid, and analysed. It furnished—

Carbon	28·42	28·08	36 =	216	27·94
Hydrogen	2·32	2·37	17	17	2·20
Nitrogen	..	..	4	56	7·25
Oxygen	..	..	20	160	20·69
Silver	41·56	..	3	324	41·92

The production of this silver compound appears to take place in the following manner:—On dissolving the nitrate of nitrotyrosine in ammonia, nitrate of ammonia and nitrotyrosine-ammonia are formed; upon the addition of solution of silver, the nitrotyrosine combines with oxide of silver, with elimination of an equivalent amount of water:—

$$C^{18}\left.\begin{matrix}H^{10}\\NO^{4}\end{matrix}\right\}NO^{6}+NO^{6}H \text{ is deprived by ammonia of } NO^{6}H.$$

$$2(C^{18}\left.\begin{matrix}H^{10}\\NO^{4}\end{matrix}\right\}NO^{6})+3AgO=C^{36}H^{17}N^{4}O^{17},3AgO+3HO.$$

It is remarkable that 2 equivs. of nitrotyrosine combine with 3 equivs. oxide of silver.

If the compound of nitrotyrosine and oxide of silver be decomposed with muriatic acid, yellow acicular crystals of muriate of nitrotyrosine are obtained.

The 3 equivs. nitrogen in the nitrate of nitrotyrosine are contained in it in three different forms; the one equivalent is that of the tyrosine, the second in the form of NO^4, and the third as nitric acid. The latter may be separated or replaced by muriatic or sulphuric acid.

Other compounds may be prepared from the nitrate of nitrotyrosine, but these from want of material I have not further examined. Its aqueous solution gives, after the addition of ammonia, orange flakes with acetate of lead, with acetate of copper a greenish-yellow, with protonitrate of mercury a greenish-white, and with the perchloride of mercury a light yellow precipitate.

The nitrate of nitrotyrosine dissolves in barytic water with a reddish-brown colour. The whole of the baryta cannot be separated from the solution by carbonic acid. On boiling with carbonate of baryta, a yellow solution is obtained, which furnishes on evaporation two kinds of crystals. A red precipitate is formed on the addition of alcohol. For preparing nitrotyrosine, the simplest plan is to take the silver compound, suspend it in water, and separate the silver by

sulphuretted hydrogen. There does not appear to be any decomposition of the nitrotyrosine under these circumstances by sulphuretted hydrogen; the liquid filtered from the sulphuret of silver left on evaporation some light yellow crystals, which under the microscope appeared to consist of star-like groups of needles; they did not furnish the reaction of nitric acid with protosulphate of iron and sulphuric acid, but they still exploded when heated with a little potash. Want of substance prevented their analysis. Notwithstanding the incompleteness of the above investigation, it results from it that nitrotyrosine enters into combination with acids and with bases, and probably likewise with salts. The combinations with acids consist, like the salts of the organic bases, of the hydrated acid *plus* nitrotyrosine. In the compounds with bases an equivalent amount of water is separated. These combining proportions entirely correspond with those observed in glycocoll and leucine.

It is a fact, which has been proved by numerous experiments, that the general character of a substance is not altered when a certain quantity of hydrogen is replaced by an equivalent quantity of hyponitric acid. The bases retain their basic properties; a neutral substance does not obtain thereby the properties of an acid; the acids retain their basicity. In another respect some change generally occurs; the basic properties of a body decrease with the entrance of NO^4, and the nitro-acid expels the acid from which it has been produced, from its compounds.

We find both the power of uniting with bases, as well as the affinity for acids, more prominently marked in nitrotyrosine than in tyrosine; from the behaviour of nitrotyrosine we are able to form an idea of that of tyrosine, and to suppose in it the same combining relations, although these compounds have hitherto not been prepared in a solid form. The supposition therefore will not prove improbable, that tyrosine, like glycocoll and leucine, constitutes a conjunct occurring in different animal substances.—Liebig's *Annalen*, Jan. 1850.

On the Amount of Nitrogen in the Fæces of Diabetic Patients.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—Dr. Percy, in concluding his paper upon the "Composition of the Fæces of Man in Health and in Diabetes Mellitus," in the last number of your valuable Journal, makes the following remark:—"Lehmann maintains that the 'fæces of diabetic patients frequently yield a mere trace of nitrogen.' (Note in Day's Trans., vol. ii. p. 377.) This is opposed to the results of Simon and myself. The odour evolved on incineration of diabetic fæces, so far as my observation has extended, has of itself uniformly afforded unequivocal proof that nitrogen is by no means deficient in these fæces. In one analysis the nitrogen amounted to 12 per cent."

In 1844 I made a vast number of experiments upon the urine of a diabetes mellitus patient, who had been suffering long and severely

from this malady; but unfortunately I only determined the nitrogen in his fæces on three consecutive occasions. The average of the three analyses gave 1·13 per cent. of nitrogen; the nitrogen in his urine at the same time being 0·64 per cent. I may add, that for the thirteen days previous to making these experiments, the patient, with the exception of one biscuit per day, was dieted on animal food divested of all exterior fat.

My per-centage is not upon the dry fæces; but were it, it would not approach the amount found by Dr. Percy, although the presumption is that the mode of living of the patient for thirteen days before making the experiment would be favourable to a high per-centage of nitrogen.

The estimation of nitrogen is not a matter of so much difficulty as to admit of the differences between Lehmann, Dr. Percy and myself (for none of us agree), to be attributable to error in experimenting. I should rather be inclined to suppose that it was owing to none of us happening to operate upon the fæces of persons at the same stage of the disease, or affected with it with like virulence. I found most unaccountable differences in the analysis of the urine, both for nitrogen and sugar, of the case I have quoted above, occur in the space of one day.

I am, Sir, your obedient Servant,

DUGALD CAMPBELL.

7 Quality Court,
Chancery Lane.

On the Formation of Aspartic Acid from Bimalate of Ammonia. By M. DESSAIGNES.

We are indebted to M. Piria for the knowledge of the interesting fact, that asparagine and aspartic acid, submitted to the oxidizing action of nitrous gas, disengage nitrogen, and leave a residue of malic acid. He thus demonstrated by analysis that these two substances may be considered as amides of malic acid, corresponding for instance to oxamide and oxaminic acid. If this be the case, we ought to be able to reproduce asparagine and aspartic acid by synthesis. The action of ammonia upon malic æther, when a method shall have been discovered for preparing this æther, ought to produce asparagine. I have not been more fortunate than my predecessors in my endeavours to obtain malic æther; but I have succeeded in preparing aspartic acid from the bimalate of ammonia.

When this salt is heated to between 320° and 392° in an oil-bath, it melts, puffs up, and disengages some slightly ammoniacal water. The residue is a transparent, resinoid, reddish mass, which dissolves but very sparingly even in boiling water. By repeated washings with hot water, an amorphous pulverulent matter, of a pale red colour and an earthy taste, is obtained. It is a new nitrogenous acid, differing in all its reactions from aspartic acid. It is a very stable substance, and dissolves in hot concentrated acids, from which it is precipitated by an addition of water unaltered, even after ebullition, for some minutes. But if heated for five or six hours with

nitric or hydrochloric acid, it undergoes a remarkable metamorphosis. The reaction is terminated when water added to the acid solution no longer causes a precipitate. The solution, evaporated to dryness in the water-bath, left a brown, very acid, crystalline residue, which is a combination of hydrochloric acid and an organic substance. This compound is readily purified by means of charcoal, and is obtained in beautiful colourless crystals. It was dissolved in a pretty large quantity of boiling water, and the solution divided into two equal parts, one of which was accurately saturated with ammonia, and the other part then added. On cooling, a quantity of minute brilliant prisms separated, which are aspartic acid. This acid does not exhibit the same crystalline form as the aspartic acid derived from asparagine; but the salts which it forms with lime, soda and the oxides of copper and silver, crystallize with the same form as the corresponding aspartates; and I have convinced myself by analysis that they contain the same amount of base. I have also submitted the isolated acid to direct analysis, and have obtained the same numbers as those furnished by the combustion of aspartic acid.—*Comptes Rendus*, March 18, 1850.

On the Action of Ammonia on the Ammonio-chloride of Platinum. *By* C. Gerhardt *and* A. Laurent.

It is well known that the ammonio-chloride of platinum, when digested with concentrated ammonia, gradually dissolves entirely without colouring the liquid. Alcohol precipitates from this solution copious white flakes, which are converted by drying into a resinous pale yellow mass, which dissolves readily in water. The alcoholic liquid contains much chloride of ammonium, and the dried resin must be again dissolved in boiling alcohol, as it also still contains much chloride of ammonium. This resin, dried at 320°, was submitted to analysis; it gave—

Platinum.....	57·9	57·4	58·2	1 =	99	58·8
Chlorine.....	22·4	..	20·4	1	35·5	21·4
Hydrogen	3·1	..	..	5	5	2·9
Nitrogen.....	15·0	..	..	2	28	16·0

These numbers approach very closely to the relation $PtCl\,N^2\,H^5$, according to which this resin would originate simply from the ammonio-chloride of platinum and ammonia by the separation of 2ClH—

$$NH^3,\,ClH + PtCl^2 + NH^3 = 2ClH + PtCl\,N^2\,H^5.$$

The analysed substance was not absolutely pure, for when heated to 320°–410°, it gave off traces of water and ammonia, and at a higher temperature disengaged muriatic acid and became insoluble. The impossibility of obtaining this substance in a regular form prevented a more accurate study of the subject. We have however proved that this substance furnishes with oxalate, sulphate and carbonate of ammonia white precipitates, which however could not be obtained in the crystallized state, and gave varying results on ana-

lysis. The precipitate produced by carbonate of ammonia disengages carbonic acid with acids. Nitrate of silver produces a precipitate in a solution of the resin, which appears to be a mixture of the chloride of silver and another platinum salt insoluble in water. But whatever may be the composition of these precipitates, with the analyses of which we have lost much time and substance, it appears to us evident that the resin is the chloride of a platinum base similar to those discovered by Gros and Reiset.—*Comptes Rends. des Trav. de Chim.*, 1849, p. 113.

On a Combination of the Chloride of Titanium with Hydrocyanic Acid. *By* F. Wöhler.

Just as the chloride of titanium has the property of combining with the perchloride of cyanogen, it also unites with anhydrous hydrocyanic acid. If some of the latter be poured upon the perchloride, combination immediately ensues, with evolution of heat and ebullition, and the two liquids are converted into a yellow powder. From the violence of the action, it is advisable to cool them previously at least down to 32°, or to pass the prussic acid in the state of gas over the perchloride contained in a tubulated retort. When it is perfectly saturated, the excess of prussic acid is distilled off at a gentle heat, and the compound sublimed by careful heating into the neck of the retort, in order to purify it from any admixture of titanic acid.

This compound is very volatile, and begins to sublime below 212°; it condenses into clear, shining, lemon-yellow crystals, similar to those of the chloride of cyanogen and titanium even in form, for they are rhombic octahedra, some simple, others with different secondary faces. Although the compound does not melt before subliming, yet the crystals, when the sublimation is quick, generally unite to a coherent mass, which on cooling falls off the glass. It fumes slightly in the air, has a strong odour of prussic acid, quickly becomes white, and soon deliquesces to a clear thick solution. It dissolves in water with considerable disengagement of heat, and with little water with evolution of gaseous prussic acid, forming a clear solution. When passed in the state of vapour through a glass tube heated to a faint red, it is decomposed, and coats the glass with copper-coloured nitruret of titanium, which is darker than usual, owing to the simultaneous separation of carbon. It is not altered by sublimation in chlorine. The hydrogen is not eliminated.

This compound consists, as shown by analysis, of 1 equiv. hydrocyanic acid and 1 equiv. perchloride of titanium $=CyH+TiCl^2$, whilst the chloride of cyanogen compound contains 2 equivs. perchloride of titanium. According to this formula, it must contain in 100 parts—

Hydrocyanic acid	22·14
Perchloride of titanium	77·86

3·962 grms. of the compound, weighed in the neck of the retort in which it had been sublimed and dissolved in water, gave, on pre-

cipitation with ammonia at a boiling temperature, 1·316 calcined titanic acid, corresponding to 3·117 grms., or 78·67 per cent. of perchloride of titanium. A compound of 2 equivs. perchloride of titanium would contain 87·55 per cent.—Liebig's *Annalen* for Feb. 1850.

On the Presence of Iodide of Cyanogen in Commercial Iodine. *By* T. Klobach.

The occurrence of iodide of cyanogen in commercial iodine had been previously noticed by F. Meyer. The author likewise observed crystals of this compound in the first crop on the sublimation of 80 lbs. of iodine. It was distilled with mercury to remove the free iodine, when 12 oz. of iodide of cyanogen, in beautiful crystals, were obtained.—*Archiv der Pharm.*, lx. p. 34.

ANALYTICAL CHEMISTRY.

On a new Reagent for detecting the Presence of Sugar in certain Liquids, and especially in Urine. *By* M. Maumené.

Several processes have been described by chemists for the detection of sugar, even under the singular circumstances of diabetic disease. Unfortunately none of the processes is of such simple execution as to be readily adopted by the medical profession. I now present chemists and physicians with a test-paper, or rather tissue, by means of which the presence of the smallest quantity of sugar can be detected in an instant.

The action of chlorine upon sugar is very imperfectly known, and the experiments which I have made with the endeavour to throw some light upon this question have made known numerous inaccuracies in the statements made by the most celebrated chemists. Thus, whatever M. Liebig may state to the contrary, chlorine acts, even in the dry state, upon sugar; it does not require a temperature of 212° to determine the reaction. At the ordinary temperature it requires more time. In all cases there is formed a brown substance, which is partly soluble in water—a caramel, which is of a brilliant black colour when dried. What is obtained with chlorine is obtained as easily, if not more so, with the chlorides, and especially with the perchlorides.

All the sugars behave like cane-sugar towards the chlorides; they all experience this dehydratation, the result of which is the brownish-black product. And this is not all; as might have been foreseen, the substances of analogous composition to that of sugar, and which like it may be represented by carbon and water, equally experience the same kind of alteration. Lignine, hemp, flax, cotton, paper and starch are thus circumstanced.

From these facts we learn the conditions under which we must

place ourselves in order to obtain a paper, or rather solid band, coated with a reagent capable of detecting the presence of sugar. Let us suppose, in fact, a slip of solid substance, which is not altered by the chloride of tin even at a high temperature; cover this substance with a layer of chloride by immersing it in a concentrated solution and desiccation; then dip the strip thus prepared in a very dilute solution of sugar, and expose it to a temperature of 266°–300° F. The part which has been immersed will immediately change colour, and will become of a brownish-black more or less deep.

As it is impossible to use paper, linen or cotton, some woollen tissue, for instance a white merino, may be employed. After having dipped the merino for three or four minutes in an aqueous solution of bichloride of tin (the oxymuriate of commerce, $SnCl^2, 5HO$), made with 100 grms. of bichloride and 200 grms. of ordinary water, let the liquid drain off, dry the merino in a piece of the same substance on the water-bath, and the reagent is prepared. It is cut into strips like the ordinary test-papers.

By means of this chlorinated merino, the physician will be able, without the least difficulty to determine whether the urine of a patient contains an appreciable trace of sugar. It will be sufficient to pour one drop of the urine upon one of these strips, and to hold it over a piece of incandescent charcoal, the flame of a lamp or of a candle, to produce in an instant a very visible black stain. The sensitiveness of the test is enormous; 10 drops of a diabetic urine, added to 100 cubic centimetres of water, furnish a liquid which turns the chlorinated merino completely brownish-black. Ordinary urine, urea and uric acid are not coloured by the chloride of tin.—*Comptes Rendus*, March 18, 1850.

On some Tests for Quinine. *By* Dr. Vogel, Jun.

A very characteristic test for sulphate of quinine has already been pointed out by Brandes. It consists in mixing a solution of sulphate of quinine with chlorine-water, and then adding caustic ammonia, when the liquid strikes an emerald-green colour. Starting from this experiment, I have succeeded, by the use of some other reagents, in producing some highly remarkable changes of colour in a solution of the sulphate of quinine.

If an excess of a concentrated solution of the ferrocyanide of potassium, instead of ammonia, is added to the solution mixed with chlorine water, a dark red colour is instantly produced, which persists some hours, but then passes into green, especially when exposed to the action of light. This reaction is highly characteristic of quinine. If caustic potash is used instead of the ammonia, the solution acquires a sulphur-yellow colour. A solution of chloride of lime mixed with muriatic acid may be advantageously substituted for the chlorine water, in which case a green powder falls on the addition of ammonia. As the above reactions do not take place with cinchonine, they may be considered as distinguishing characters of the two alkaloids.—Liebig's *Annalen*, Feb. 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Amidogen Compounds of Tungsten. *By* Prof. Wöhler.

Gay-Lussac and Thenard found, forty years ago, in their researches on the metals of the alkalies, that potassium and sodium absorb ammoniacal gas when heated; and, with the elimination of hydrogen gas, form dark olive-green compounds, which they called *azoture ammoniacal de potassium* and *de sodium*. The quantity of hydrogen which was liberated at their formation amounted to half the volume of the absorbed ammoniacal gas, therefore 1 equivalent. With water they were exactly decomposed into hydrate of the alkali and ammonia; and when heated were converted into ammoniacal gas and a nitruret of the metal, which was likewise decomposed by water into hydrate of the alkali and ammonia, and must consequently have been K^3N or Na^3N. We may conclude from these facts, as Berzelius and Gmelin have shown, that these olive-coloured bodies are the amidogen compounds of potassium and sodium $=KNH^2$ and $NaNH^2$.

This deportment of the alkaline metals towards ammonia, to which hitherto little attention has been paid, is for this reason remarkable, that it may enable us to form a correct judgement of the nature of some compounds which the author has obtained by the action of ammoniacal gas upon heated tungstic acid or heated protochloride of tungsten, and which will be described in the following pages. No nitruret of tungsten was obtained according to expectation, but substances which must be considered, from their behaviour and their composition, as amidogen compounds of tungsten.

Nitretamide of Tungsten, or the combination of nitruret of tungsten with amidide of tungsten, was obtained by the action of ammoniacal gas upon the protochloride of tungsten, WCl^2. The protochloride was prepared directly by burning metallic tungsten in chlorine free from air. It was quickly conveyed into a long dry glass tube, and exposed in this to a current of dry ammonia, the tube being frequently turned. Without the assistance of external heat the protochloride becomes so hot that it partially melts, and the chloride of ammonium formed begins to volatilize and covers the surface of the protochloride; when this spontaneous action had ceased, the further decomposition was completed by placing some

incandescent charcoal under the tube, taking care however that the heat became scarcely stronger than requisite to volatilize the chloride of ammonium. When, in this manner, the whole of the chlorine, as well as of the sal-ammoniac, had been expelled, and no further trace of the latter was formed, the tube was let cool, the current of ammoniacal gas being still continued.

The product of this action is a black substance, caked together, as if partially melted from the fusion of the protochloride, which occurs at its formation, and possessing great lustre in this more dense state, like that of the carbon separated from gas at a strong red heat.

When heated in the air, it disengages ammoniacal gas long before incandescence, then takes fire, and burns into yellow tungstic acid. When heated in a porcelain crucible, placed between recently-calcined charcoal powder, it parts with the whole of the nitrogen and hydrogen at about the melting-point of silver, and leaves pure gray metallic tungsten. It behaves in the same manner at a faint red heat in dry hydrogen, with formation of a quantity of ammonia.

Fused with hydrate of potash, it is converted into tungstate, with disengagement of ammonia and hydrogen. Acids and solutions of the alkalies have no action upon it. As, notwithstanding every care in its preparation, it was usually found to contain some traces of protochloride or of the chloride of ammonium most tenaciously, in order to obtain it pure for analysis, it was treated with dilute solution of potash or ammonia, and then perfectly washed.

The amount of tungsten in it was determined partly by burning it into acid, and partly by reducing it to metal alone or in hydrogen. The experiments were made with substance of different preparations, and likewise with substance of the same preparation, but taken from different parts in the tube. In twelve determinations the amount of tungsten was found to be between 86·76 per cent. as minimum and 90·80 per cent. as maximum. The quantities of hydrogen and nitrogen taken together, and constituting the loss, varied consequently between 13·24 and 9·20.

These differences arise from the circumstance, that the compound, on being heated alone, but especially in hydrogen, most readily parts with nitrogen and hydrogen in the form of ammonia, and is converted into another compound with a greater amount of tungsten. But at its formation the portions situated furthest from the entering current of ammonia are at the same time exposed to the action of free hydrogen gas, as hydrogen is liberated in the formation of the compound; and moreover it possesses the property, in a highly remarkable degree, of producing the decomposition of the ammoniacal gas into its constituents at a temperature at which alone in a glass tube it would certainly not be decomposed.

That kind of the compound which had given 90·80 tungsten furnished, on calcination with soda-lime, a quantity of ammonio-chloride of platinum, which corresponded to 8·26 per cent. nitrogen.

For the estimation of the tungsten, the substance was used in

quantities of 2·0 to 0·5 grm.; in the estimation of the nitrogen, 2·463 grms. of ammonio-chloride of platinum were obtained.

Wöhler is led to conclude, from the results of these analyses, that there exist two very similar combinations between nitruret of tungsten and amidide of tungsten, of which one $=2WN+WNH^2$, the other $=W^2N+WNH^2$.

The compound $2WN+WNH^2$ contains—

		According to the formula.	Found.
Tungsten	..	86·58	86·76
Nitrogen	12·81	13·42	13·24
Hydrogen	0·61		

At its formation decomposition takes place between $3WCl^3$ and $9NH^3$, and furnish $W^3N^3H^2$ $(=2WN+WNH^2)$, $6NH^4Cl$ and 1H as gas.

When this compound is heated to a certain temperature in hydrogen, 1 equiv. nitrogen is removed as ammonia, and a second compound is formed $=W^2N+WNH^2$, which is distinguished externally by the grayish colour of its powder. This second compound consists of—

	According to the formula.	Found.
Tungsten	90·44	90·80
Nitrogen.....	8·92	8·24
Hydrogen	0·64	

The first compound experiences a similar change when heated alone, but in this case varying mixtures originate, evidently according to the temperature. Both furnish pure metal at a strong red heat.

These compounds cannot be produced in the moist way. Protochloride of tungsten, as formerly observed by the author, is dissolved by a concentrated solution of ammonia, with evolution of hydrogen and formation of tungstate.

Oxynitretamide of Tungsten, $3WN+W^2NH^2+2WO^2$.—This compound is formed by the action of gaseous ammonia upon heated tungstic acid. It is however very difficult to obtain it of constant composition, as it parts with nitrogen and hydrogen at a higher temperature, both in an atmosphere of hydrogen and alone. The tungstic acid used for its preparation was prepared by calcining the crystallized salt of ammonia. The acid, reduced to a fine powder, was spread out in a thin layer in a long glass tube, and heated, but scarcely to perceptible redness, in a current of dry ammonia until not a trace more water was formed. In this operation it was also observed that this compound exerts a very decomposing action upon the ammonia at a temperature at which alone it would certainly not be decomposed. If the operation is made in a porcelain tube at the melting-point of silver, only metallic tungsten or varying mixtures of this and the compound are obtained.

This compound is of a pure black colour. If the unpulverized acid in pseudomorphous crystals of the ammonia salt is used for its preparation, it is likewise obtained pseudomorphous in black scales,

which have a semi-metallic lustre. On heating the salt to redness, it disengages ammonia. Acids and alkalies have no action upon it. Solution of potash only disengages some ammonia, and extracts some tungstic acid if the metamorphosis has not been quite complete. Hypochlorite of soda dissolves it, with evolution of nitrogen and the odour of chloride of nitrogen, and forms a tungstate. Heated in the air, it burns with a lively incandescence to yellow tungstic acid. Heated with oxide of copper or minium, it burns with a faint incandescence, a property however which the pure oxide and the metal itself possess. Exposed to a strong red heat in hydrogen, it is completely reduced to metal, with formation of ammonia and water. It is not altered by being heated in a sealed tube with water to 446° F. The amount of tungsten was determined in some cases by burning the compound into acid, in others by reduction with hydrogen. In nine experiments with substance, most frequently of different preparation, and in part with quantities of several grammes, 87·65 per cent. of tungsten as minimum and 88·47 per cent. as maximum were found; consequently there remained for the nitrogen, hydrogen and oxygen (constituting the loss), 12·35 per cent. as maximum and 11·33 per cent. as minimum.

The mean from these nine determinations is 88·03 per cent. tungsten, and 12·04 for the other constituents, the direct determination of which gave the following data.

1·1805 grm. of the substance furnished, on reduction in hydrogen in a porcelain tube which was connected with a small tube filled with fragments of hydrate of potash, 0·073 water, corresponding to 5·49 per cent. oxygen.

In this case 1·0395 grm., or 88·05 per cent. of gray metal, were obtained. The entire loss in weight therefore amounted to 11·95 per cent.

In another experiment 0·887 grm. substance gave 0·038 water, corresponding to 3·80 per cent. oxygen. The mean from these two numbers is 4·64.

Several other experiments, which were made with smaller quantities of substance of different preparations, all gave a higher amount of oxygen, which may have arisen from the presence of some free oxide, and perhaps also from the moisture of the hydrogen gas, although passed through sulphuric acid, and afterwards through chloride of calcium, to dry it.

To determine the amount of nitrogen, 1·403 grm. substance was calcined with soda-lime; it furnished 1·587 grm. ammonio-chloride of platinum, corresponding to 7·15 per cent. nitrogen.

To determine the hydrogen, 1·383 grm. substance was mixed with a large excess of recently-calcined, half-decomposed minium, the tube repeatedly exhausted at 122°, and heated to redness again. By this means only 0·025 grm. water was obtained, corresponding to 0·20 per cent. hydrogen.

The disagreement of the numbers found for the nitrogen and hydrogen with those which the author regards as the probably correct ones, is undoubtedly owing to the circumstance that the com-

pound of itself very readily parts with ammonia when not heated in an atmosphere of ammonia.

At all events, these analytical results, compared with the behaviour of the substance and its origin, appear to agree with no other more probable composition than that above expressed by the formula, according to which it would consist of—

	According to the formula.	Found.
Tungsten	88·04	88·03
Nitrogen.....	7·44	7·15
Hydrogen	0·27	0·20
Oxygen	4·25	4·64

The reciprocal decomposition between tungstic acid and ammonia is consequently not so simple as would have been expected from the composition of the two, according to which from 1 equiv. tungstic acid and 1 equiv. ammonia there might be formed exactly 3 equivs. water and 1 equiv. nitruret of tungsten $=WN$, which latter would contain 87·11 per cent., or pretty nearly the same amount of tungsten as the compound which is actually formed.

This, or a very similar oxygenous compound, is produced when tungstate of potash is mixed with an excess of chloride of ammonium, covered with a layer of chloride of potassium, and fused at a strong red heat in a platinum crucible. On dissolving the mass in water, and extracting with a dilute solution of caustic potash any undecomposed acid tungstate, this compound is left behind as a heavy coal-black substance. When magnified a hundred times, it is seen to consist of dark iron-black particles with a metallic lustre. This is the same body which Wöhler described twenty-six years ago as black oxide of tungsten. But it contains both nitrogen and hydrogen, and liberates a quantity of ammonia, not only when fused with hydrate of potash, but even when heated alone. This presence of hydrogen is inexplicable when we consider the production of this body at a strong red heat, unless we assume that it is assimilated in the treatment with water on isolating the compound, and that it is formed from another substance. It is also remarkable, that, when exposed in a closed vessel to a bright white heat, it leaves pure metal. In other respects it behaves precisely like that prepared directly with ammoniacal gas. Wöhler found from 88 to 89 per cent. of tungsten in it, but it always left from 1 to 2 per cent. of potash, in the treatment with chlorine, when the tungsten is volatilized as protochloride and acichloride.

When tungstate of soda is fused with chloride of ammonium under a layer of common salt, and the mass is then treated with water and solution of caustic potash, a blackish-brown product is obtained, which is seen under the microscope to consist of a mixture of an iron-black and a dark copper-red substance. The latter is probably the tungstate of the oxide of tungsten and soda, formerly described by the author. By exposing brown oxide of tungsten in ammoniacal gas to a gentle red heat, we also obtain a product containing nitrogen and hydrogen, but mixed with unaltered oxide, as

evident from the brownish-black colour. Pure metal is obtained on heating to a strong red in a porcelain tube.

Berzelius's statement, that oxide of tungsten is reduced to metal, at a strong red heat, by hydrogen, is not confirmed by Wöhler. According to his observation, tungstic acid is only reduced to oxide at a temperature above the melting-point of silver, and is then not further changed. That statement probably refers to an oxide containing alkali. The pure oxide of tungsten is of a beautiful brown colour with a violet tint. Under a magnifying power of 100 it appears to have a metallic lustre, like the colour of gun-metal, and caked together as if crystalline. The author did not succeed in obtaining a nitruret of tungsten free from hydrogen. By heating tungstic acid to redness in cyanogen, there was formed, with the liberation of much carbonic oxide, a black substance of a semi-metallic lustre, which disengaged with hydrate of potash but little ammonia, and contained therefore nitrogen; but it was mixed intimately with carbon, as evinced by combustion in chlorine. It contained 94·5 per cent. of metal.—*Göttingen Nachrichten*, 1850, p. 55.

Chemical Notices. By Prof. Schönbein.

I. *On the Decomposition of the Iodide of Potassium in the Dry Way.*—The metallic acids with 5, 3 and 2 atoms of oxygen decompose iodide of potassium in the dry way. Arsenic acid decomposes it on trituration with it. On raising the temperature, iodine is set free, arseniate of potash and arsenious acid being formed—

$$3AsO^5+2KI=2KO\ AsO^5+AsO^3+2I.$$

If the temperature does not attain the point of volatilization of AsO^3 only iodine sublimes, but otherwise some arsenious acid also. An aqueous solution of arsenic acid decomposes iodide of potassium pretty quickly with the assistance of heat. Antimonic acid disengages dense vapours of iodine from iodide of potassium. Chromic acid and bichromate of potash eliminate iodine from the iodide of potassium even in the cold; on the application of heat, dense vapours of iodine escape, and the residue consists of chromate of potash and oxide of chromium. When bichromate of potash is used, we have—

$$5KO,\ 2CO^3+3KI=8KO\ CrO^3+Cr^2\ O^3+3I.$$

3 parts by weight of the bichromate suffice therefore to separate the iodine contained in 2 parts by weight of iodide of potassium. The residue is a dirty green mass, which parts with neutral chromate of potash to water, leaving behind oxide of chromium. The bichromate of potash can therefore be used to prepare iodine in the dry way from the iodide of potassium. The method is not expensive, as neutral chromate of potash is reobtained from the residue. Molybdic acid separates iodine even in the cold, and abundantly at a moderate heat, undoubtedly with the formation of molybdate of potash and molybdic oxide. Tungstic acid behaves like molybdic acid; stannic acid, the two artificially prepared isomeric modifica-

tions as well as the native ore, tinstone, mixed intimately with iodide of potassium, separate iodine on the application of heat, probably with formation of stannate of potash and protoxide of tin. Titanic acid and uranic acid exhibit a similar behaviour.

The acids of the metalloids, phosphorus, silicon and boron, likewise separate iodine from iodide of potassium in the dry way. If dry powdered iodide of potassium is conveyed into fused anhydrous phosphoric acid, a most violent disengagement of iodine takes place; and if the experiment is made in an open platinum crucible, a flame makes its appearance, which, seen through the simultaneously-liberated vapours of iodine, exhibits a crimson-red colour, and is but of short duration. The fused hydrate of phosphorus ($HO + PO^5$) also separates abundantly the vapours of iodine from the iodide of potassium, with the appearance of flame. At the same time, however, a pretty large amount of iodurette hydrogen is eliminated. This reaction probably takes place according to the following equation—

$$3PO^5 + 2KI = 2KO, PO^5 + PO^3 + 2I;$$

and the flame proceeds from the combustion of the phosphorous acid produced and vaporized by the high temperature.

Silicic acid distinctly eliminates vapours of iodine from iodide of potassium at a high temperature, and with the access of atmospheric air or of oxygen; but no iodine is disengaged in carbonic acid, hydrogen or nitrogen when the tube is strongly heated; but when atmospheric air or oxygen is substituted for these gases, iodine is eliminated the more quickly the higher the temperature of the mixture. Boracic acid behaves in like manner. On the other hand, the previously-mentioned acids decompose the iodide of potassium even with total exclusion of the air.

Compounds of the Peroxide of Iron.—Anhydrous perchloride of iron, mixed with iodide of potassium, liberates iodine at the ordinary temperature, which is disengaged on the application of heat in dense vapours; chloride of potassium and protochloride of iron are formed. A highly concentrated solution of the perchloride of iron precipitates from an equally strong solution of iodide of potassium a large portion of the iodine in a crystalline form, with production of chloride of potassium and protochloride of iron—

$$Fe^2 Cl^3 + KI = 2FeCl + KCl + I.$$

The persulphate of iron, $Fe^2 O^3, 3SO^3$, behaves in a similar manner. On moderately heating the dry mixture, dense vapours of iodine are given off without any sulphurous acid. 3 equivs. sulphuric acid, previously diluted strongly with water, and incapable of separating alone any iodine from iodide of potassium, when poured over a mixture of 1 equiv. peroxide of iron and 1 equiv. iodide of potassium, liberate copious vapours of iodine on ebullition; and when these have ceased to appear, the residue contains only sulphate of the protoxide of iron and sulphate of potash. It is evident therefore that $Fe^2 O^3 + 3SO^3 + KI$ are changed into $FeO, SO^3 + KO, SO^3 + I$. Peroxide of iron may therefore be employed just as well as the per-

oxide of manganese for separating iodine from iodide of potassium. All the salts of the peroxide of iron behave in the same manner.

Ferridcyanide of potassium, mixed with iodide of potassium, fumes; no iodine is liberated on the application of heat, but products are formed which the author has not yet examined.

Salts of the Peroxide of Copper.—The action of the persalts of copper upon iodide of potassium is known; the solid anhydrous persalts of copper, even the carbonate, liberate iodine from the iodide of potassium on the application of heat.

II. *Decomposition of the Bromide of Potassium in the Dry Way.*—In general those substances which separate iodine from iodide of potassium likewise liberate bromine from the bromide of potassium, never however with the same ease. Bichromate of potash and peroxide of iron are most effective; the latter may likewise be used in the dissolved state to obtain the bromine from bromide of potassium by distillation. The fused hydrate of phosphoric acid liberates little bromine and much bromide of hydrogen; silicic or boracic acid, heated with bromide of potassium with the access of oxygen, furnishes no bromine.

III. *Decomposition of Chlorides in the Dry Way.*—The chlorides resist the action of the above-mentioned agents most; chloride of potassium or sodium, mixed with any of the above-mentioned substances, which decompose the iodide or bromide of potassium, liberates no chlorine even on the application of a strong heat; but the chlorides of barium, strontium, calcium, magnesium, and probably of some other metals, do. This separation of chlorine is best effected by the bichromate of potash. A perceptible quantity of chlorine is liberated from an intimate and perfectly dry mixture of this salt and chloride of calcium at an elevated temperature, with formation of neutral chromate of potash and lime and oxide of chromium. Apparently all those chlorides behave in this manner, which, when heated in the air, part with some chlorine, whilst a portion of their metal is oxidized by the oxygen of the atmosphere.—Poggendorff's *Annalen*, lxxviii. p. 513.

On a Method of preparing large Quantities of Metacetonic Acid. *By* Dr. F. Keller.

In an experiment made to ascertain the acids formed on the contact of flour-paste with animal membrane, the paste mordants of the white-leather tanners, I obtained a large amount of metacetonic acid, instead of acetic acid and butyric acid, as I had expected. The small quantity in which this interesting acid, the existence of which had been questioned until a recent period, is obtained in other and more circuitous ways, rendered the following process very desirable. A given portion of wheat paste (2 to 3 lbs.) is mixed with ten times its weight of water at 122°–140° into a paste, and then with a fourth part of coarsely-cut waste leather, and after the addition of powdered chalk, left in a warm spot to ferment. In the course of three or four weeks in winter, in a few days in summer, the process

is terminated, which is known by the sinking together of the previously spongy mass. It is strained, washed out with hot water, converted into soda salt, evaporated, and the acid separated by sulphuric acid. To separate the acids which I suspected it to contain, a portion was saturated with carbonate of soda, the remainder added, and distilled from the saline residue. This proved to be a mixture of acetate and metacetonate of soda. In all further experiments to discover any other acid besides the metacetonic, the silver salts prepared from the residues exhibited the same composition. The silver salt furnished 59·25–58·96 and 59·32 per cent. of metallic silver. The metacetonate of silver contains according to theory 59·55 per cent. The salt furnished, on combustion with oxide of copper—

Carbon	19·73	6	19·89
Hydrogen	2·72	5	2·76
Silver	59·32	1	59·55
Oxygen	18·23	4	17·80

The recently-precipitated silver salt could be recrystallized from hot water without any very great amount of blackening; but once dried over sulphuric acid, it is decomposed for the greater part on ebullition with water.

The lead salt, prepared by saturating the pure acid with hydrated oxide of lead, forms a radiately-crystalline mass, which melts by the warmth of the hand to a viscid liquid.

The baryta salt dried to a gummy mass, which after some time swelled up into cauliflower-like heads, which effloresced and fell to powder in the air. The salt contains 36·38 per cent. water of crystallization (9 atoms), which it loses on being heated to 284°. It furnished 54·42 per cent. of baryta.

The soda salt was only once obtained in crystals after it had been heated to melting, and dissolved in as little water as possible. In general it was obtained as a tallow-like mass. All the salts exhibited the rotatory motion of the butyrates when thrown in small fragments upon water.—Liebig's *Annalen*, Feb. p. 205.

On the Fibrine of Muscular Fibre. *By* J. Liebig.

When finely-divided flesh is freed, by exhaustion with cold water and pressure, from the matters soluble in this menstruum, a white tasteless residue is left, which consists of true muscular fibre, nerves and cellular tissue. Muscular fibre is usually considered to be identical with the fibrine of blood; but this is an error, which has probably arisen solely from their similarity in physical properties. When the fibrine of blood is immersed in water containing one-tenth of muriatic acid, in a short time it swells into a gelatinous mass; on the addition of stronger acid, the jelly contracts nearly to its original volume, and again swells in water like a sponge. This experiment may be repeated several times without any perceptible quantity of the fibrine becoming dissolved in the liquid.

The fibrine of muscular fibre is quite different in this respect.

When placed in water containing the above amount of acid, the greater portion dissolves immediately and perfectly, forming a liquid which is slightly turbid from the presence of fatty matters, and which is with difficulty separated completely from the undissolved portions by filtration, although this may be perfectly effected. This solution takes place at ordinary temperatures. The solution coagulates when neutralized, forming a thick, white, gelatinous paste, which is readily soluble in excess of alkalies; chloride of sodium and other saline solutions produce a coagulum in it, which dissolves in a large quantity of water.

The precipitate obtained on neutralizing the muriatic acid of the fibrine of muscle is soluble in lime-water, and the solution when boiled yields a coagulum just like a dilute solution of albumen. If the precipitate has been previously boiled with water, it is insoluble in lime-water. But the most remarkable fact is, that this constituent of muscle, which is so readily soluble in dilute muriatic acid, exists in very different proportions in different kinds of animals; thus *e.g.* the muscular fibre of poultry and oxen is almost entirely soluble; whilst in the case of the muscular substance of sheep, more than half, and in that of the calf far more than this proportion, remains undissolved. This insoluble residue is elastic and white; but it is more gelatinous and softer than the fibrine of blood which has become swollen in slightly acidified water.

The fibrine of muscle especially differs in composition from that of blood in the amount of nitrogen contained in it; it approximates to that of albumen. The following analyses were made by M. Strecker.

Fibrine of the flesh of the fowl, dissolved in muriatic acid, precipitated by ammonia, and dried at 248° F., I. II. III. and IV.

Fibrine of the flesh of the ox, V. Fibrine of the flesh of the sheep, VI. VII. and VIII.:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Carbon		54·46	..	..	53·67			
Hydrogen ..		7·28	..	..	7·27			
Nitrogen.. ..		..	15·84	..	..	..	..	16·26
Sulphur		..	..	1·21	..	1·02	1·11	
Oxygen								
Ash.....	1·4							

The fibrine constitutes a fractional portion of a per cent. only of the blood; in accordance with those analyses which are most to be depended upon, it contains more nitrogen than the fibrine of muscle, which renders the notion that it might serve for the formation of the latter very problematical. The iron, which is never absent, forms an important constituent of the fibrine of the blood. I have not been able in any manner to obtain fibrine of the blood free from iron. It has been concluded, from the colour of the ash left on its incineration, which is sometimes perfectly white, that iron was absent: but even this white ash contains a considerable amount of iron

When blood-fibrine, which has been well washed, is covered with water in a well-stoppered vessel, and kept in a warm place, putrefaction soon ensues. It gradually becomes disintegrated, assuming at the same time a deepish colour, and in about three weeks is almost entirely dissolved, forming a slightly-coloured liquid, in which some black flakes are suspended, the colour of which arises from sulphuret of iron; the latter may be readily separated by filtration. The solution thus obtained cannot be distinguished from a solution of albumen; it coagulates by heat, forming a gelatinous mass, which has all the properties, as also the composition of albumen, as shown by the following analyses made by Dr. Strecker at my request:—

	I.	II.	III.	IV.	V.
Carbon	53·9				
Hydrogen	6·99				
Nitrogen	..	15·58			
Sulphur.....	..	..	1·59	1·45	
Oxygen					
Ash	..	..	..	..	0·28

This albumen is one of the most remarkable products of putrefaction. During the decomposition a highly fœtid volatile product is formed, with a very small quantity of free hydrogen. The liquid filtered from the coagulated albumen contains a small quantity of a nitrogenous substance, which has not yet been further examined.—*Ann. der Chem. und Pharm.*, January 1850.

On the Composition of Mellon and the Mellonides.
By C. Gerhardt.

A few years ago I attacked the theory according to which mellon was considered to be a compound radical similar to cyanogen, and the mellonides salts similar to the cyanides, as being full of error. In a paper which I published on this subject with M. Laurent, it was demonstrated that mellon contains, besides carbon and nitrogen, 1·5 per cent. of hydrogen, the composition of mellon being $C^6 N^9 H^3$, and not $C^6 N^8$, as had heretofore been believed. We have since repeated the analysis of this substance, prepared by calcining the sulphocyanide of mercury, and we have arrived at the same result. This sulphocyanide, like several other salts of mercury, contains water of crystallization, of which it cannot be deprived without complete decomposition.

We also found, as stated in that paper, that by causing boiling potash to act upon mellon, no hydromellonic acid is produced, but another tribasic acid containing $C^6 N^8 H^4 O^2$. With respect to the composition of the mellonides, which are obtained from the sulphocyanide of potassium at a red heat, we had reserved the question, not having sufficient material to determine it. One fact, however, appeared to result from our experiments, and that was the presence of hydrogen in the dry mellonides, among others in the mellonide of silver dried at 284°.

Notwithstanding the numerous arguments which we brought forward, the majority of chemists nevertheless continue to regard mellon and the mellonides as non-hydrogenated substances.

At present the question appears in my opinion to be solved. M. Henneberg has recently published some experiments, which I think completely decide in favour of my opinion. He has found that both mellon and the mellonides yield the same identical acid by treatment with boiling potash, with disengagement of ammonia. But M. Henneberg has mistaken the composition of this acid, which is the very one that M. Laurent and myself represented by the formula $C^6 N^3 H^4 O^2$, the neutral salts being $C^6 N^3 HM^3 O^2$. I beg that chemists will themselves verify these relations, which they will find exact, and which prove, in my opinion—

1. That mellon is the imide (the acid salt of ammonia less 2 equivs. of water) of the preceding acid, and presents consequently the composition $C^6 N^9 H^3$.

2. That the mellonides are compounds similar to the metallic salts, which are obtained with several imides (for instance with phtalimide, succinamide, &c.), *i. e.* the mellonides represent mellon in which H^2 is replaced by M^2.

3. That consequently the dualistic theory of mellon and the mellonides has no foundation, as I have always maintained.—*Comptes Rendus*, March 1850.

Researches on the light Oils obtained in the Distillation of Wood. *By* A. Cahours.

When water is mixed with the crude wood-spirit of commerce, a pale yellow oil separates and comes to the surface. This is not an immediate, pure and definite product; when submitted to distillation, it begins to boil at about 194°, while the last portions do not distil over at a lower temperature than 392°. The elementary analysis and the density of the vapour having led to no definite result for any of these products, I agitated the crude oil with concentrated sulphuric acid, and obtained a brownish-red viscous mass, and a supernatant clear liquid of an aromatic odour. This, washed with dilute alkaline solution, dried over fused chloride of calcium, and then distilled over anhydrous phosphoric acid, begins to boil at 226°; the last portions pass over between 320° and 338°. A considerable portion of the product distilled over between 226° and 234°; it was kept apart. I also obtained several fixed points, one from 262° to 266°, another from 293° to 298°, and a third from 327° to 334°.

The product which boils between 226° and 230° is toluene (benzoene of Deville), $C^{14} H^8$. The mean of several experiments on the density of the vapour was found to be 3·27, which represents 4 vols. of vapour, and agrees perfectly with the theoretical density, 3·24. In order to demonstrate completely the identity of this product with toluene, I treated it with fuming nitric acid. I obtained mononitrated toluine and binitrated toluine; the first, acted upon by an

alcoholic solution of hydrosulphate of ammonia, yielded toluidine, having all the properties assigned to it by M. Hofmann. The second is converted, under the influence of the same reagent, into a new alkaloid, nitrotoluidine, having the formula $C^{14}\,H^{8}\,N^{2}\,O^{4}$. This alkaloid, which crystallizes in yellow needles, gives with hydrochloric, nitric, sulphuric and phosphoric acids, well-defined compounds, to which analysis assigns the following formulæ:—

Hydrochlorate	$ClH, C^{14}\,H^{8}\,N^{2}\,O^{4}$.
Nitrate	$NO^{5}, C^{14}\,H^{8}\,N^{2}\,O^{4}\,HO$.
Sulphate	$SO^{3}, C^{14}\,H^{8}\,N^{2}\,O^{4}\,HO$.

When treated with the chloride of benzoyle and cumyle, it moreover furnishes compounds analogous to the amides and the anilides.

The product which boils between 262° and 266° exhibits considerable analogy in its properties with toluine; in composition it differs only by containing $C^{2}\,H^{2}$ more; it is therefore a homologue of that substance. Several analyses and three determinations of the density of vapour agreeing perfectly with each other, led to the formula $C^{16}\,H^{10}$=4 vols of vapour. I shall call it *xylene*; treated with fuming nitric acid, this substance yields products analogous to those furnished by toluine. The *mononitrated xylene*, dissolved in alcohol and treated with hydrosulphate of ammonia, gives a base analogous to toluidine, which I have named *xylidine*.

The liquid which boils at 298° exhibits all the characters and the composition of cumene, $C^{18}\,H^{12}$. The analyses and the determinations of the density of the vapour entirely agree with this formula. In order to demonstrate the identity of this substance with cumene, I treated it with fuming nitric acid, and obtained two compounds which exhibit all the properties of mononitrated and binitrated cumene: these, treated with hydrosulphate of ammonia, furnished cumidine and nitrocumidine.

On this occasion I submitted to examination mesitylene, regarded by Sir Robert Kane, its discoverer, as the radical of the compounds derived from acetone. Having admitted, in accordance with the researches of Sir R. Kane, that pure mesitylene boiled between 266° and 275°, I ten years ago prepared this product; and the determination of the density of the vapour of this substance, which was only a mixture, led me to double its formula. The recent researches of M. Hofmann on this subject having led him to triple the formula of this compound, I considered it my duty to take up the subject afresh. I consequently prepared a large quantity of this product; the greater portion of the liquid obtained boiled between 324° and 327°. The density of the vapour, taken twice upon different samples, furnished perfectly accordant results, leading to the formula admitted by M. Hofmann, $C^{18}\,H^{12}$. It is consequently an isomeric compound of cumene, but not identical with that body; for besides differing in a remarkable manner by its boiling-point, it yields, in contact with reagents, entirely different products. Under the influence of fuming nitric acid, it furnishes three distinct products, viz.

1. Mononitrated mesitylene, by avoiding an excess of acid and carefully cooling.

2. Binitrated mesitylene, discovered by M. Hofmann, by using more acid and allowing the temperature to rise.

3. Trinitrated mesitylene (the formation and properties of which I have already described) by substituting a mixture of nitric and fuming sulphuric acid for the nitric acid.

These three products, derived by the substitution of hyponitric vapour for hydrogen, may be formulated as follows:—

$$C^{18}\,\frac{H^{11}}{(NO^4)'} \qquad C^{18}\,\frac{H^{10}}{(NO^4)^2} \qquad C^{18}\,\frac{H^{9}}{(NO^4)^3}$$

The first of these bodies, the mononitrated mesitylene, when treated with an alcoholic solution of potash, evolves heat and disengages two products on distillation. One liquid is obtained in very small quantity, and possesses the property of an alkaloid; the second, which is solid, dissolves very readily in alcohol, and crystallizes from it in beautiful prisms by spontaneous evaporation. This product furnished on analysis results leading to the formula $C^{18}H^{11}NO^4$. It is consequently isomeric with mononitrated mesitylene.

With respect to the last carburetted hydrogen, obtained in the treatment of the volatile oil of wood by sulphuric acid, and which boils between 327° and 334°, it possesses exactly the same composition as cumene and mesitylene. It also exhibits the same state of condensation as those bodies, without being identical with either.

The volatile oil produced in the destruction of wood, and which contaminates the wood-spirit of commerce, contains therefore the same hydrocarbons as are produced in the distillation of coal-tar, and which have been recently examined by Charles Mansfield. These results consequently establish an intimate connexion between coal and the ligneous matter from which it is considered to be derived. In some samples of wood-spirit I found a far more volatile oil than the preceding one; it begins to boil at about 137°, and the last portions distil over between 194° and 212°. This very volatile oil is composed almost entirely of two substances; one, constituting about three-fourths, is the acetate of methylene, as I have proved by elementary analysis, the determination of the density of the vapour, and various reactions; the other possesses the properties and the composition of the metacetonate of M. Fremy, $C^{12}H^{10}O^2$=4 vols. of vapour.—*Comptes Rendus*, March 1850.

On the Existence of Iodine in Freshwater Plants.
By M. Chatin.

In verifying the fact, pointed out by Muller*, of the presence of iodine in a cress, the origin of which was unknown, I was led to discover—

That iodine exists in the water-cress, and that it is not peculiar

* Lindley's Vegetable Kingdom, p. 363.

to this species, nor general in the plants belonging to the family of the Cruciferæ.

That iodine is absent, or at all events cannot be detected in terrestrial plants, whilst it exists in all aquatic plants.

That, among the latter, those which grow in running waters contain more iodine than those from stagnant waters.

That, in ponds of sufficient extent to be violently agitated by the wind, the plants approach in this respect more to those in running water.

That the proportion of iodine contained in plants is in general independent of their nature, and solely subordinate to their habitat, as shown by the *Confervæ*, *Potamogeton*, *Nymphææ*, *Ranunculi*, cresses, &c., which are all equally rich in iodine in running waters, and all equally poor in ponds and marshes.

That the iodine exists in the state of alkaline iodide dissolved in the juices of the plant, and not combined with the tissue.

Among the plants analysed, and on which are founded the preceding results, are enumerated,—*Alyssum saxatile*, the cabbage, *Capsella bursa pastoris*, *Erysimum*, *Cheiranthus Cheiri*, the horseradish, and radish—terrestrial cruciferæ which contain no iodine; and of the various aquatic plants containing more or less iodine, the cress, *Nasturtium amphibium*, *Conferva crispata*, *Chara fœtida*, *Fontinalis antipyretica*, *Typha angustifolia* and *minima*, *Scirpus lacustris*, *Arundo phragmites*, *Acorus calamus*, *Sagittaria*, *Nymphæa*, *Potamogeton crispum* and *P. pectinatum*, *Mentha aquatilis*, *Veronica beccabunga*, *Phellandrium aquaticum*, *Gratiola*, *Ranunculus aquatilis*.

As it is found not only in the plants growing in large rivers, as the Seine, the Marne and the Isere, but in those from every rivulet, pond or marsh, it is impossible that it can be derived from any mineral spring, but must be widely diffused over the earth, accompanying like a satellite the chlorides, with which it is extracted by the water. If the plants from running waters contain more iodine than those from stagnant, it is because they have an indefinite reservoir to go to, where the liquid exhausted of iodine is immediately replaced by fresh.

The presence of iodine explains the anti-scrofulous and anti-tuberculous properties, &c. of the cress, *Veronica beccabunga*, *Phellandrium*, &c., and the preference given to those plants which grow in running waters.

The analysis consisted in carefully incinerating the plants, exhausting the ash with boiling water, and ascertaining the presence of iodine by the use of starch, sulphuric acid, nitric acid, and the nitrate of potash and sulphuric acid. The decoloration of the liquids and the volatilization of the iodine by the application of heat were always used in confirmation of the result. According to the quantity of iodine, the plants furnished either an immediate and intense violet colour, or the same colour after a certain time, or a purple-violet colour either immediately or after a certain lapse of time.

In these operations certain precautions are necessary; for instance,

the plant, before being incinerated, should be moistened with a solution of caustic potash to prevent the loss of a portion of the iodine, whilst the inconvenience resulting from the fusibility, communicated to the ash by this addition, must be borne in mind, as also the property which saline mixtures have, especially those containing a large amount of carbonates, of masking more or less completely the reactions, especially that of chlorine.—*Comptes Rendus*, March 25, 1850.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

March 30, 1850. Anniversary Meeting. (The President in the Chair.)

The Report of the Council and the audited Account of the Treasurer were read, and the Society proceeded to the election of Council and Officers for the ensuing year, when the following gentlemen were declared to be duly elected:—

President.—Richard Phillips.

Vice-Presidents.—William Thomas Brande; Lyon Playfair, Ph.D.; Thomas Graham; W. A. Miller, M.D.

Secretaries.—Robert Warington and Benjamin Brodie.

Foreign Secretary.—A. W. Hofmann, Ph.D.

Treasurer.—Robert Porrett.

Council.—Thomas Andrews, M.D.; John Blyth, M.D.; William Ferguson; J. J. Griffin; H. Bence Jones, M.D.; J. P. Joule; G. D. Longstaff, M.D.; Th. Redwood; Edward Schunck, Ph.D.; E. F. Teschemacher; E. Frankland, Ph.D.; A. W. Williamson, Ph.D.

The thanks of the Society were voted to the President, Officers and Council for their services during the past year. The Secretary read a list of the contributions towards defraying the expenses of the charter; when Professor Graham proposed, and Dr. Longstaff seconded, a vote of thanks to the contributors.

Royal Irish Academy.

Jan. 28, 1850. (John Anster, LL.D., Vice-President, in the Chair.)

Mr. Donovan read a "Notice of the Analysis of certain gold-coloured Bronze Antiquities found at Dowris, near Parsonstown, in the King's County."

At a late meeting of the Academy, a communication was made by Thomas L. Cooke, Esq., of Parsonstown, relative to certain ancient bronze articles found at Dowris in the King's County. Some specimens having been, by that gentleman, placed in my hands for analysis, I deem it proper to lay before the Academy the results of my investigation. The articles given to me were part of a celt and a portion of a horn.

The golden hue of these ancient bronzes suggested to some persons the idea that they contained an admixture of zinc, an ingredient not hitherto, I believe, found to enter into their composition. Such bronzes in the British Museum as have been analysed consist of copper and tin only; and the Greek and Roman bronze coins are known to have been composed of the same metals. Bishop Watson, it is true, supposed that zinc constituted a part of a celt examined by him, his proof being that the metal, when melted, emitted a thick white smoke, accompanied by a blue flame, which are esteemed, he says, certain marks of zinc. This may possibly have been the case in Bishop Watson's particular specimen; but the celts examined by other chemists proved destitute of zinc, and its introduction into the ancient bronzes must have been a very rare practice. Zinc would no doubt enhance the colour and increase the malleability of the compound; but it would lessen its hardness, one of the chief qualities for which the metal was valued. Add to this, the test assigned of the presence of zinc is equivocal. Dr. Pearson observed a fume, to a small amount, when portions of an ancient bronze, which he proved not to contain zinc, were strongly heated; and he quotes the statements of certain assayers, who observed fumes to arise from charges of lead with silver, or lead with gold and silver, when much air was admitted. He also says, that "if much air be admitted to the alloy of copper with tin in fusion, a white smoke will sometimes be seen."

The specific gravity of the celt was 8·767, an indication of the presence of tin and of the absence of zinc; but to determine the question the following process was adopted :—

A portion of the metal was dissolved by heat in nitric acid; a white powder separated, which being edulcorated, dried and mixed with borax and incinerated pitch, was exposed to the heat of a Russian furnace. The black mass obtained from the crucible, when viewed with a strong magnifier, disclosed thousands of metallic particles disseminated through it. By pulverizing and washing this matter, I obtained a portion of the metal. Its solution in muriatic acid, mixed with a small quantity of nitric acid, afforded those appearances with solution of gold which indicate tin. The nitric solution of the celt, from which tin had been thus separated, was subjected to the action of a bright plate of lead immersed in it; the whole of the copper was thus precipitated, as was proved by the test of ammonia. The filtered liquor, now deprived of copper and tin, was mixed with solution of sulphate of soda, and boiled down to a small bulk. The sulphate of lead being filtered off, solution of potash was added, but no oxide of zinc appeared.

Thus it was proved that the celt did not contain zinc; other trials, however, showed that it contained a little lead. In order to determine the proportions of the constituent metals, the following method was adopted. I believe it is one which differs in some respects from that hitherto practised, but previous trials convinced me that in such cases it is necessary.

100 grs. of celt metal were introduced into a tubulated retort, to which were attached a receiver and a series of three very small

Woulfe's bottles, each of which contained a little liquid ammonia; the receiver was empty. $1\frac{1}{2}$ oz. measure of pure nitric acid being poured through the tubulature of the retort, and a spirit-lamp applied, a violent effervescence ensued; everything dissolved except the tin, which became peroxidated. Some acid and much nitrous gas came over, the latter of which passed through the ammonia. When the celt metal had all disappeared, the contents of the Woulfe's bottles were mixed with those of the receiver; the resulting liquor was of a light blue colour, for the nitrous gas had carried over with it some copper; it was reserved for a future process.

The solution of nitrate of copper was diluted with distilled water, and introduced into a precipitating glass, in order that the peroxide of tin should subside. When this happened, the perfectly transparent solution of copper was decanted, and the peroxide of tin was digested with a little nitric acid, in order to dissolve away minute particles of copper, which sometimes escape solution by being entangled in the peroxide of tin. The peroxide was then well edulcorated with frequent affusions of distilled water. The collected washings were evaporated to one eighth, and a minute quantity of peroxide of tin was thus recovered, which was added to the rest. By proper management the peroxide was drained to the last drop, dried on the capsule, collected with great care on glazed hot paper, and thence transferred to a bulbed tube of Bohemian glass, without the smallest loss. The bulbed tube had been previously heated and counterpoised in the scale-pan of the balance. The bulb was then gradually heated until the peroxide was red-hot; the weight of the peroxide of tin was 16·678 grs., equivalent, according to the estimate of Berzelius, to 13·112 grs. of metallic tin. This mode of determining the quantity of peroxide of tin I found much better than filtering and burning the filter.

In order to discover the quantity of lead, pure sulphate of soda, in quantity known to be more than sufficient, was added to the solution of nitrate of copper. No precipitate ensued. The whole was introduced into a retort, a receiver was attached, and the acidulous water was distilled off. The process required the greatest vigilance, for the least increase of heat towards the end caused the liquid to sputter and shoot out particles in all directions, a circumstance which had imposed on me the necessity of abandoning a former analysis of this celt. At length the nitrate of copper showed a tendency to solidify; the heat was then raised until nitrous gas began to appear. The heat being withdrawn, some distilled water was added, which dissolved the nitrate of copper, but left a small quantity of sulphate of lead. This being washed with frequent small portions of distilled water, was separated in the same manner as the peroxide of tin had been, and heated to an obscure red. Before it had cooled entirely, it was ascertained to weigh 1·75 gr., which, according to the estimate of Berzelius, indicated 1·142 gr. of metallic lead.

The next step was to ascertain the quantity of copper. The washings of the sulphate of lead were added to the solution of nitrate of copper; the whole was distilled in a retort, with the same pre-

cautions as before, until the nitrate showed a tendency to solidify. At this period I connected the same series of Woulfe's bottles, still containing the ammonia, which had been used for condensing the nitrous vapour, and which also held a little copper dissolved. Through this ammonia the nitrous gas evolved from the nitrate of copper, now undergoing decomposition in the retort, was obliged to pass, previously to its emission into the atmosphere, in its passage transferring to the ammonia the chief part of the copper which it had carried over. The heat was gradually raised, and continued until the nitrate of copper was converted into a black mass.

I have mentioned that the *chief part* of the volatilized copper was detained by the ammonia, but it was not entirely absorbed; for, at the latter end of the decomposition of the nitrate of copper, the flame of a spirit-lamp, held in the fumes which escaped from the issue-tube of the Woulfe's bottles, assumed a splendid green colour. The loss in this way must be trivial.

The bottom of the retort which contained the black mass was now cut out by means of a red-hot tobacco-pipe, and the black matter detached from the glass. But so obstinately did a very small portion adhere, that it could only be removed by nitric acid; the nitrate thus formed was decomposed by heat, and the resulting black matter was added to the main product.

In order to recover the copper which was contained in the Woulfe's bottles and receiver, the liquors were collected and distilled to a very small bulk. The distilled liquor was colourless, and therefore contained no copper. The residue, being transferred into a capsule, was decomposed by heat, and the very small quantity of black matter which resulted was added to the main product.

The total quantity of black matter was now heated red-hot, by means of a Russian furnace, for about five minutes. Before it cooled, its weight was ascertained to be 106·767 grs., equivalent, according to the estimate of Berzelius, to 85·232 grs. of metallic copper.

In another analysis of the same celt, I confirmed the foregoing result by a different proceeding, which was as follows:—100 grs. of the metal having been dissolved in nitric acid, and freed from tin and lead as before, the solution of nitrate of copper was precipitated by an excess of pure potash. By boiling the mixture, the peroxide of copper resulted, and this was boiled with repeated affusions of distilled water. The washings were evaporated to a small quantity, and thus a little more peroxide of copper was obtained. The whole product was filtered and dried. The filter was carefully burned on a saucer, the peroxide was heated red-hot for five minutes, and, after deducting the known weight of the ashes of the filter, the weight of the peroxide was ascertained to be 0·41 less than by the former method; but I rely more on the former estimate.

Directed by some preliminary experiments on the celt metal, I dissolved 100 grs. in 2 oz. by measure of pure muriatic acid, mixed with one-eighth of pure nitric acid, over a lamp-heat. A black powder was separated, which, when dried and thrown on a plate of platinum, maintained at a red heat over a spirit-lamp, burned with

the characteristic blue flame of sulphur, in the midst of which could be discovered a few sparkles of burning charcoal. The sulphur had not been discovered in the former analysis, because the nitric acid being concentrated acidified it. The weight of this black powder was but 0·15 gr. Although I sought for traces of gold under the supposition that the celt might have been gilt, as some persons supposed, I could not obtain any distinct evidence of the presence of that metal.

I next proceeded to the analysis of the horn, and conducted it with the same care. It is unnecessary to say anything more on the subject than to state the result of the two analyses. The celt consisted of—

Copper	85·232
Tin	13·112
Lead	1·142
Sulphur and carbon	0·150
	99·636
Loss	0·364
	100·000

And the horn consisted of—

Copper	79·345
Tin	10·873
Lead	9·115
	99·333
Loss	0·667
	100·000

The loss in both cases may be partly accounted for by the escape of copper in the nitrous gas, as already mentioned, which it was not in my power to prevent. The proportion of lead in the celt is so small that advantage to the properties of the alloy could scarcely be derived from it, yet it is too great to suppose that the lead was a mere impurity of the copper. I believe antiquarians are not agreed with regard to the purpose to which celts were applied. Whatever it was, the composition of the one examined by me was admirably calculated for fabricating weapons. The metal admitted of a fine polish, and was then of a beautiful colour. Its toughness was so great that it was capable of sustaining the fiercest encounter without fracture; while its edge, by the mere process of hammering, became so hard and keen that it would cut not only through flesh, but bone. It was a matter of great interest to me to discover the skilful proportions of the constituent metals, which, in times of remote antiquity, our ancestors employed in order to combine beauty with utility; and both of these objects they appear to have fully accomplished.

In conclusion, I have to observe, that as the results of my analyses differ more or less from others which have been stated by chemists, I have been thus particular in detailing my methods. The difference of our results only proves the variety of proportions in which ancient manufacturers manipulated.

THE CHEMICAL GAZETTE.

No. CLXXXII.—May 15, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Occurrence of a Substance related to Xanthic Oxide in the Animal System. *By* Prof. SCHERER.

AT the request of my colleague, Prof. Kölliker, who had constantly found in his anatomico-microscopical investigations of the spleen the liquids of this organ to possess an acid reaction, I examined this important physiological organ, especially for lactic acid, and the volatile acids discovered by me in the fluids of the flesh. The mode of examination was exactly similar to that first adopted by Liebig in his researches on flesh, with the modification adopted by me in my investigation of bullock's heart, viz. first separating the kreatine by crystallization, freeing the residual liquid from baryta by sulphuric acid, and after removal of the sulphate of baryta distilling off the volatile acids.

In the examination of the spleen of the ox, the hacked mass had to be exhausted with boiling water instead of pressure, as it became so gelatinous after agitation with water that very little liquid could be obtained by pressure. The mucilaginous gelatinous mass passes through the meshes of the linen bags, and completely stops them. It is readily exhausted with boiling water, which has merely the inconvenience that some gelatine also dissolves, which causes the liquid to gelatinize on concentration. The light red-coloured decoction, mixed with barytic water, immediately gives a copious precipitate like the fluids of muscular flesh. On evaporating the filtrate, the excess of baryta separates as carbonate, but with it (and which is also the case with the precipitate of phosphate of baryta, and most copiously with the sulphate of baryta on the subsequent addition of sulphuric acid) two other organic bodies, which dissolve in dilute boiling caustic potash, from which they are precipitated for the greater part by muriatic and also by carbonic acid.

The precipitate produced by these acids appeared under the microscope to consist chiefly of a fine crystalline mass, in which, after long contact with muriatic acid, some distinct and large yellowish-coloured crystals became perceptible. The principal mass of the precipitate however retains its crystalline angular nature, without its being possible to detect, even with the highest magnifying power, any distinct form of crystal. As the larger distinct crystals

appeared to have some resemblance to the several forms of uric acid, I treated a portion of the precipitate upon platinum foil with nitric acid, and obtained, on cautious evaporation at the margin of the residue, the characteristic red colour of that body, and which, on being moistened with ammonia, changed into the brilliant purple colour of murexide.

The chief mass of the residue, after treatment with nitric acid, was of an intense yellow colour; and since, owing to the entire removal of the albumen by coagulation, and from the crystalline nature of the precipitate as well as the very pale yellow colour of the residue, it could not be considered to be xanthoproteic acid, it was conceived that the colour might possibly arise from xanthic oxide or guanine. And, in fact, the yellow residue, on being mixed with a solution of hydrate of potash, distinctly exhibited the most beautiful red-yellow coloration.

The whole of the crystalline precipitate obtained was on this account again dissolved in solution of potash, and mixed with chloride of ammonium, to precipitate the uric acid. After standing for a short time, it separated in the state of gelatinous urate of ammonia, and the filtered liquid deposited on gentle evaporation the new substance as a yellowish-white crystalline powder. This was collected upon a filter, and again dissolved in ammonia, to remove the last portions of uric acid: it dissolves very readily in ammonia. On evaporating the ammoniacal solution in the water-bath, it left a laminar mass, which could be readily detached, and which, on being tested with nitric acid, left a purely yellow stain on evaporation, thus proving to be entirely free from uric acid, as also on solution in potash (when it disengaged very little ammonia) and mixture with chloride of ammonium, and likewise on precipitating the alkaline solution with excess of muriatic acid, and examining the precipitate under the microscope after it had stood for some time.

The entire mass obtained by evaporating the ammoniacal solution was once more dissolved in dilute caustic potash, and precipitated by a current of pure carbonic acid. The filtered white crystalline powder, well washed with cold water, was free from potash, and did not form *hard* pieces when dry, as stated by Liebig and Wöhler of xanthic oxide, but *remained crystalline, pulverulent,* and was easily reduced to a fine powder *without* acquiring a *waxy lustre,* nor does it dissolve in nitric acid without but *with* disengagement of gas. In cold muriatic acid it is almost insoluble, and in boiling but sparingly soluble. On cooling, the muriatic solution deposits it for the greater part as a fine powder, no crystals being formed as in the case of guanine. It dissolves in concentrated sulphuric acid without any blackening or evolution of gas. On dilution with water, the liquid first becomes slightly turbid, but this disappears on the addition of more water. Diluted with hot water, the sulphuric solution does not furnish any crystals on cooling.

This substance is very sparingly soluble in cold water; one part requires 1090 parts water; it dissolves in much larger quantity in

boiling water (1 in 180), and the solution on cooling deposits the excess as an exceedingly fine powder, which adheres firmly to the glass. The aqueous solution has no action upon vegetable colours. It also dissolves somewhat in boiling alcohol, but is again deposited from the filtered solution on cooling. As above stated, it dissolves in boiling nitric acid with disengagement of gas, and white crystals form as the solution cools, which are scarcely soluble in cold, but readily in hot water, from which they again crystallize unaltered. From want of material, I could not pursue further the examination of this interesting product of decomposition. A boiling solution of it, mixed with a boiling solution of carbonate of ammonia, does not change its colour in the least. On ebullition with peroxide of lead, a slight evolution of gas takes place; and on concentrating the filtered liquid and cooling, minute verrucoid groups of yellowish crystals separate, which appear under the microscope to be composed of a large number of delicate acicular crystals. The substance, after drying in the water-bath, lost nothing more in weight when heated up to 248° F., and was not altered in the least. In the qualitative determination of the nitrogen, the relation of nitrogen to the carbonic acid was found to be as 1 : 2·5, consequently the same as in xanthic oxide. On analysis it furnished—

Carbon	44·257	5 =	30	44·117
Hydrogen.....	3·219	2	2	2·941
Nitrogen	40·820	2	28	41·176
Oxygen.....	11·704	1	8	11·766

leading to the formula $C^5 H^2 N^2 O$, which differs essentially from that of xanthic oxide and guanine.

From this analysis and the calculated formula, it follows that this new substance is xanthic oxide —1 equiv. O, and differs consequently from uric acid, $C^5 H^2 N^2 O^3$, by containing 2 equivs. O less.

I would propose for this new substance the name *hypoxanthine*. Its close affinity to xanthic oxide is moreover rendered certain by the fact, that both furnish, as the final product of their treatment with nitric acid, the same yellow body, which acquires a red colour with potash. The occurrence of this substance simultaneously with uric acid, which is so closely related to it in composition, is certainly interesting. I did not consider it requisite to submit this latter to elementary analysis, although I obtained the requisite quantity in a pure state. Its characteristic reactions were exhibited so distinctly with the precipitate obtained from the potash solution by chloride of ammonium, that I thought it superfluous.

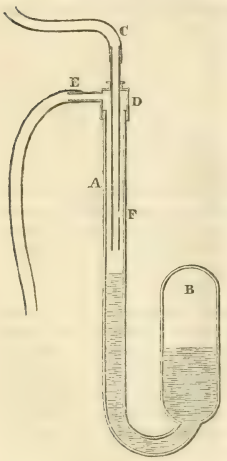
Hypoxanthine does not occur only in the ox. I have found it in the human spleen at all periods of age, and likewise in the substance of the heart; and frequently in such quantity in the latter, that it separates spontaneously as the decoction cools, or remains suspended in the liquid. The other results obtained in the examination of the spleen, in particular those relating to the volatile acids present and the absence of kreatine, I reserve for a future communication.—Liebig's *Annalen*, March 1850.

Description of an Apparatus for regulating the Heat produced by a Gas-burner. By ALEXANDER KEMP, *Assistant Chemical Teacher in the University of Edinburgh* *.

Any one who has had occasion to maintain an object at a regulated temperature for a length of time by means of a gas-burner, must have experienced the difficulty of keeping the heat at the required point from two causes. First, the quantity of gas passing through the burner in any given time varies directly as the pressure on the service-pipes; a greater quantity is therefore consumed when the pressure increases, and the amount of heat applied to the object is increased in the same degree.

Secondly, as the temperature of the atmosphere is liable to change during the continuance of the experiments, its cooling influence will be greater at one time than another. Both these causes conduce to render the attainment of the object in view one of considerable difficulty.

It will be evident, from what I have just stated, that any instrument intended to supply the desideratum must be self-acting, and must supply the gas to be consumed exactly as it is required. The instrument I have been in the habit of using for some time back consists of an air-thermometer, AB, containing mercury in the lower part of the bulb B and part of the stem A. A tube of smaller diameter, marked C, passes down the axis of the tube A, the annular space being made air-tight by a small brass stuffing-box, D, by means of which it may be retained at any required elevation. In using the instrument, the bulb B is placed in the same situation as the body to be exposed to the heat of the gas-flame; for instance, if it is a water-bath containing vessels or other objects, it is immersed in the water; or if an air-chamber or hot-press, it is placed as near the object as possible, so that the air in the bulb may attain the same temperature as the surrounding medium.



A tube of vulcanized India rubber is now to be connected with a stop-cock attached to the service-pipe, and its other extremity drawn over the end of the pipe C, which will make it sufficiently air-tight. A second India rubber tube is in like manner to be attached at E, to convey the gas to the burner employed as a source of heat in the operation.

* Communicated by the Author.

Let us now suppose that it is required to keep an object at a temperature of 100° F., the bulb of the instrument being placed contiguous to the object; the stop-cock is to be opened so as to allow a free supply of gas to the burner, which is now to be kindled; the heat now begins to act on the air contained in the ball of the instrument, causing it to expand and force the mercury up the stem A; when it is found, by the use of a common thermometer, that the heat has risen to 100°, the tube C is to be pushed down till its lower extremity is immersed in the mercury. This would, of course, cause the flame to be extinguished; but, to prevent this occurring, a small hole is bored through the inner tube opposite F, which permits a small quantity of gas to pass to the burner. As the passage of the gas is now interrupted, the source of heat is withdrawn, and the cooling influence of the surrounding air comes into play, which will cause the air contained in B to contract and the mercury to sink in A, leaving the end of C uncovered, and thus open a free passage to the gas, which by its combustion would again raise the temperature so as to cut off the supply; but in a very short time these two opposing forces come to an equilibrium, and the flame scarcely varies in size.

After trying the instrument in the form described, I experienced a practical difficulty from the want of perfect contact between the end of the tube C and the mercury, from which I found that it might rise many degrees beyond the assigned limit without sufficiently lowering the flame; this I at once saw might be overcome by making the tube of a substance which would become *wetted* by the mercury. I tried a brass and also a copper tube, amalgamated at the end, but they slowly dissolved in the mercury, which they rendered impure, so that its rise and fall could not be depended on with the required nicety. The substance now used is platinum, of which about half an inch of the lower end of the tube is formed, amalgamated by dipping it into a liquid amalgam of sodium and mercury. In connexion with this I may mention, that platinum, iron and steel may be readily amalgamated in the same way, or by using a strong solution of caustic potash or soda in contact with the mercury.

I have now used several of these instruments for various periods, and have found them to answer well. In one operation, conducted in Professor Gregory's laboratory (the fermentation of sugar into butyric acid), one of them has been in use for upwards of six weeks, keeping about five gallons of liquid at a temperature of 98° F., and it has not been observed to vary. I have also another in an apparatus for artificial incubation, where the temperature in the well part is kept at 120° F. For this latter purpose I consider it well adapted, as it may be placed in the vessel along with the eggs, and thus the use of hot water be altogether dispensed with, as well as the constant attendance required to regulate the heat applied to the eggs.

I need not take up space with pointing out many applications that may be made of the instrument; these will occur to every one: but there is one I may allude to, viz. obtaining products of the de-

composition of organic bodies at fixed temperatures, which has hitherto been somewhat difficult, as different substances are formed as the temperature varies to which they are subjected. The only limit to its application is the same as in the ordinary thermometer, viz. the boiling of the mercury; this might be overcome by using an easily fusible metal, such as tin, and constructing the instrument of iron, when its form might also be modified to suit particular circumstances.

On the Behaviour of Cuminic Acid in the Organism. *By* Dr. Hofmann.

The observations of M. Schlossberger on the physiological effects of organic substances of analogous constitution, have reminded me of some experiments made some years ago, but which other occupations had prevented me from publishing. The investigation of the derivatives of cuminic acid (cumole, nitrocumole, cumidine, cuminonitrile, &c.), by exhibiting the remarkable analogy of cuminic and benzoic acid, suggested the idea of examining the action of the first of these acids upon the animal system. Mr. Ure had made the important observation, that benzoic acid is soon converted into hippuric acid in its passage through the body. Erdmann and Marchand had found that cinnamic acid, introduced into the system, experiences the same transformation. This last observation has been recently confirmed by Wöhler and Frerichs, who found that the ingestion of the balsam of Peru always gives rise to the production of a certain quantity of hippuric acid proportionate to the cinnamic acid which it contains. This observation is readily explained by the easy conversion of cinnamic acid into benzoic acid under the influence of oxidizing bodies.

The conversion of cuminic acid, the homologue of benzoic acid, into hippuric acid, was not so probable. In fact, cuminic acid has hitherto only been converted into benzoic acid by very indirect methods; for instance, by the oxidation of its hydrocarbon, cumole, by nitric acid. It might appear far more probable that there would be formed, in the passage of cuminic acid through the body, an acid homologous with hippuric acid, a glycocuminic acid. It was the hope of realizing such a metamorphosis which led me to undertake the experiments I am about to describe, although they did not answer my expectations.

After having perfectly satisfied myself of the harmlessness of cuminic acid upon rabbits, I took over-night several grammes of this acid without experiencing the least disagreeable sensation. Several other persons took part in these experiments, so that I was very soon able to collect the requisite quantity of urine for these researches. The urine, concentrated in the water-bath to a syrupy consistence, deposited some yellow needles, which, after purification by animal charcoal and recrystallization, exhibited all the characters and the composition of cuminic acid. They furnished on analysis—

Carbon	72·66	20 =	120	73·17
Hydrogen.....	7·37	12	12	7·31
Oxygen.....	..	4	32	19·48

From the preceding, it results that cuminic acid experiences no alteration in its passage through the body. The experiment was twice repeated with the same result; and the whole of the cuminic acid taken, with the exception of a trifling quantity, was found again in the urine. It was impossible to detect, besides cuminic acid, any other acid derived from it.

The unsuccessful result of this experiment did not prevent my making some trials with an acid, which is still more closely related to benzoic acid than even cuminic acid itself. This is the toluylic acid discovered by Mr. Noad. In fact, whilst the formula of cuminic acid is distinguished from that of benzoic acid by $3C^2H^2$, that of the toluylic acid differs only by C^2H^2:—

Cuminic acid	$C^{20}H^{12}O^4$
?.....	$C^{18}H^{10}O^4$
Toluylic acid	$C^{16}H^8O^4$
Benzoic acid	$C^{14}H^6O^4$.

Toluylic acid was taken in the dose of several grammes without any bad consequences, but it was impossible to find it again as such in the urine. This gave up to æther a small quantity of a neutral substance, forming very regular and very minute crystals; but the substance is formed in such small quantity, and the preparation of the toluylic acid is so troublesome, that I have been compelled to discontinue these experiments.—*Journ. der Pharm.*, April 1850.

On several new Combinations of Ammonia with the Ferrocyanides, and especially with the Ferrocyanide of Nickel. By A. Reynoso.

When an excess of ammonia is added to recently precipitated and moist ferrocyanide of nickel, it is seen first to dissolve, then to change colour, and almost immediately to produce a precipitate composed of a multitude of very minute needles of a violet colour. To obtain this compound in a dry state, fit for analysis, is extremely difficult, owing to its great instability; mere exposure to the air decomposes it into ferrocyanide of nickel and ammonia, which escapes. On passing a current of dry air over the salt, it is decomposed, leaving ferrocyanide of nickel in the tube. Nor was it possible to dry it by passing a current of dry ammoniacal gas over the salt, although the experiment was continued for three days. I finally succeeded by the following method:—A considerable quantity of the salt was prepared, and after being well washed with water containing ammonia, it was left freely exposed to the air for two days upon a filter. The portion which was in contact with the air was entirely decomposed, but in the centre of the mass was a quantity of undecomposed salt in violet-blue acicular crystals. The compound once dry is more stable; it is no longer decomposed by exposure to the air, but when heated to 212°–302° F. it parts with

water and ammonia. The residue however is not ferrocyanide of nickel, as it disengages ammonia and hydrocyanate of ammonia at a higher temperature, leaving pyrophoric carburets, which detonate, take fire, and burn in the air like a fusee.

If the moist salt is boiled with water, it is decomposed into ferrocyanide of nickel, water and ammonia. The ferrocyanide of nickel obtained in this way is perfectly pure, and this method of preparing it is the only one which yields it free from cyanide of potassium. When prepared by precipitating a salt of nickel with the ferrocyanide of potassium, it leaves an alkaline ash even after having been washed with hot water for several days. It is not requisite to boil this compound with water, for the decomposition of the ammoniacal ferrocyanide of nickel takes place at the ordinary temperature, only it requires much more time. Weak acids remove the ammonia without attacking the ferrocyanide of nickel. Strong acids decompose the ferrocyanide of nickel in the ordinary manner. Potash disengages ammonia, produces a precipitate of oxide of nickel and ferrocyanide of potassium.

The ammoniacal ferrocyanide of nickel may also be prepared by pouring ferrocyanide of potassium into a solution of nickel containing much ammonia, or by pouring a solution of a salt of nickel into a mixture of ammonia and ferrocyanide of potassium. In all cases the crystals are the more beautiful the more slowly they are formed, that is when there is much ammonia present, and the solution is consequently very weak. The analysis of this salt led to the formula $2NiCy, FeCy, 5NH^3, 4HO$.

Biammoniacal Ferrocyanide of Nickel, $2NiCy, FeCy, 2NH^3, HO$. —On pouring ferrocyanide of potassium into a solution of ammoniacal nitrate of nickel, a greenish-white precipitate is obtained, which, when well dried, forms a very deep green mass, which yields a white powder. It adheres to the tongue, and is quite insipid, is wholly insoluble and unalterable in water. Weak acids act upon it in the same manner as upon the preceding salt, but it is less easily decomposed. Ammonia dissolves it, and converts it into the preceding salt. When heated, it disengages ammonia, cyanide of ammonium, and leaves a carburet, which fuses in burning.

This salt combines, or rather mixes with the ammoniacal ferrocyanide of copper, furnishing a precipitate of a beautiful peach-blossom colour. The best method of obtaining it is to precipitate a mixture of ammoniacal nitrate of nickel and nitrate of copper by the ferrocyanide of potassium.

Bi-ammoniacal Ferridcyanide of Nickel.—Ferridcyanide of potassium produces, in an ammoniacal solution of nitrate of nickel, a beautiful yellow precipitate, soluble in an excess of ammonia, and having the formula $3NiCy, Fe^2 Cy^3, 2NH^3, HO$.

All the ferro- and ferridcyanides of the metals whose oxides are soluble in ammonia are themselves soluble in ammonia. The alkaline solution of the ferridcyanide of cobalt is of a very deep red colour; those of the protoxide of manganese and of the protoxide of iron, which are insoluble in ammonia, must be excepted. But

these oxides only dissolve in ammonia with the aid of an ammoniacal salt.

The ferro- and the ferridcyanides of the metals whose oxides are soluble in potash are themselves soluble in potash. Thus, for instance, potash added to the ferrocyanide of zinc produces at first ferrocyanide of potassium and oxide of zinc, which dissolves in the excess of the potash. If the potash is added with precaution, on filtering, the liquid contains only ferrocyanide of potassium, oxide of zinc remaining on the filter. With the ferrocyanide of mercury the reaction is also very distinct: this compound is white; on treatment with potash, ferrocyanide of potassium is formed, and yellow oxide of mercury, insoluble in an excess of potash.—*Comptes Rendus*, April 8, 1850.

Notes on the Purification and Properties of Chloroform. By* William Gregory, M.D., *Professor of Chemistry in the University of Edinburgh*†.

1. Chloroform has been prepared both from alcohol and wood-spirit. The latter has been used for the sake of cheapness; but as it is a mixture of several liquids, all of which do not yield chloroform, it gives an impure product, in a proportion which varies much, but is always below that obtained from alcohol. There is therefore not only no advantage, but the contrary, in using wood-spirit, which is not, after all, much cheaper than alcohol.

2. But the chloroform from these two liquids, *when fully purified*, is quite identical in all its properties. Its smell, density, boiling-point and action in the system are in both cases exactly the same. That from alcohol is no doubt more easily purified than the other, but it also contains certain volatile oily impurities, which must be removed before it can be safely used. The peculiar oils which adhere to both kinds of chloroform are not identical, or at least not all identical, but they are of analogous constitution and properties.

3. Soubeiran and Mialhe have examined these oils. They contain chlorine, have a disagreeable smell, and when inspired or smelt cause distressing headache and sickness. In the case of wood-spirit, some of its own impurities distil over unchanged, and are also found in the chloroform.

4. It is well known that many persons, after the use of chloroform, have suffered from headache, nausea, and even vomiting, as I have more than once seen. Headache and nausea I have myself often experienced, when I have tried different specimens of chloroform, without taking so much as to produce the full effect.

5. Perfectly pure chloroform does not, so far as I have seen or experienced, produce these disagreeable effects. It is therefore

* Although I am alone responsible for the opinions contained in this paper, it is my duty to state, that all the experiments and observations mentioned in it have been made by me in concert with my able assistant, Mr. Alexander Kemp, of whose ingenuity and accuracy I have had constant opportunities of judging.

† Read before the Royal Society of Edinburgh, March 1850.

highly probable that when they occur, as they do with some individuals, from the use of chloroform of more than the average goodness of quality, they depend on the presence of a trace of these poisonous oils.

6. All good manufacturers of chloroform purify it by the action of oil of vitriol, which destroys the oils, while at the same time a part of the acid is reduced to sulphurous acid. The chloroform, to remove this, is then distilled with lime or carbonate of baryta, and is tolerably pure if the process be well conducted.

7. But it is not quite pure, and contains a trace, more or less distinct, of the oils. I have found this to be the case with all the best chloroform made here up to 1849; and I have several times seen headache and sickness from the use of such chloroform, which was the best anywhere made. I must add, however, that the quantity of oils in the chloroform of the best Edinburgh manufacturers, although variable within certain limits, was always so small, that that product was fit for use, and only caused headache, &c. in a few peculiarly sensitive persons.

8. It was desirable to have a test for these impurities, as well as an easy and effectual mode of removing the last traces of them, especially as many sorts of chloroform not made here were far inferior in quality to that prepared in Edinburgh. One very delicate test is, that oil of vitriol, which should be quite colourless, pure, and of the full density of 1·840 at least, as it may be obtained by Mr. Kemp's process, lately read to the Royal Society, when agitated with the chloroform, becomes yellow or brown, from its action on the oils, which it chars and destroys. Any change of colour is easily seen by contrast with the colourless chloroform which floats above. Pure chloroform gives no colour to the acid. It is essential that the oil of vitriol be colourless and also of full density; for if coloured, it is not easy to see a slight change on its colour; and if below the proper density, that is too weak, it is not much coloured by a chloroform which will render dark brown the acid of proper strength.

9. Another test, still more delicate, I find to be the smell of the oils. When chloroform is poured on the hand or on a handkerchief, it rapidly evaporates; but the oils, being less volatile, are left behind; and their smell, previously covered by that of the chloroform, is easily recognized. Until very lately no chloroform was sold, or indeed known, which would stand this test, or even the former.

10. Up to 1849 the best commercial chloroform had a specific gravity of 1·480, which was considered a guarantee of its purity; but it had been obtained by chemists of specific gravity 1·494, and even 1·497. I have found that chloroform of 1·480, when once more acted on by oil of vitriol, which destroys the oils and becomes brown, may be obtained, after removing the sulphurous acid, of specific gravity 1·500 at 60°. This I take to be the specific gravity of pure chloroform. Our best makers have lately, much to their credit, pushed the purification so far as to furnish chloroform even of this highest density, and also in other respects such as it ought to be.

11. There are still however many makers in other places whose chloroform is not so pure ; and I shall now describe the method which, with Mr. Kemp, I have employed for purifying, perfectly and easily, any commercial chloroform, except one remarkable specimen—a process which will enable any medical man to purify it for himself with the greatest facility.

12. The chloroform, having been tested as above, and found more or less impure, is to be agitated with oil of vitriol (half its volume will be sufficient), and *allowed to remain in contact* with the acid, of course in a clean, dry, stoppered bottle, and with *occasional agitation* till the acid no longer becomes darker in colour. As long as the action is incomplete, there will be seen, after rest, at the line of contact, a darker ring. When this no longer appears, the chloroform may be drawn off, and for greater security once more acted on by a quarter of its volume of the acid, which should now remain colourless. It is now to be once more drawn off, and in a dry stoppered bottle mixed with a little powdered peroxide of manganese, with which it is gently agitated, and left in contact until the odour of sulphurous acid is entirely destroyed and the chloroform has acquired a mild, agreeable, fruity smell. It has then only to be poured off into a proper phial. It will now leave no disagreeable smell when evaporated on the hand. [If the commercial chloroform, after having been *frequently well shaken* and *left for some time in contact* with the acid, has given to it only a moderate tinge of colour, it is probable that it may be completely purified by the first process. To ascertain this, test a fresh portion in a tube with fresh acid, shaking well and allowing it to stand some time. If it do not colour the acid at all, then the whole chloroform has only to be finally purified by the oxide of manganese. If the acid become coloured in the test-tube, it will be as well to act on the whole chloroform a second time with fresh acid till it stands the test. Mr. Kemp has observed, in repeating this process for me, the very curious fact, that as soon as the action is complete and the oily impurities are destroyed, but not sooner, the chloroform tested with the acid in a tube, exhibits a strongly convex surface downwards, where it rests on the pure acid, or, what is the same thing, the acid becomes concave at its upper surface. The smallest trace of impurity, not sufficient to affect the density of the chloroform, we have found to render the line of junction horizontal. It is probable that this may become a valuable test of the perfect purity of chloroform ; but we shall not say more on this subject until we have thoroughly examined it.] This process requires no apparatus beyond a few stoppered bottles and a pipette, if we wish to draw off the whole chloroform without loss, although nearly the whole may be simply poured off. The use of the oxide of manganese is due to Mr. Kemp ; and on the large scale the chloroform may be filtered through a cylinder full of it. In this final purification of commercial chloroform, no distillation is necessary. Indeed no rectification is required at all, if it be well washed with water before using the acid.

13. It may be considered as certain, that the use of chloroform

thus purified will very rarely, if ever, cause the disagreeable effects above noticed*. As to more serious bad results from the use of chloroform, so often spoken of elsewhere, it is enough to state that a large proportion of the cases must be attributed to the use of a liquid so impure as hardly to deserve the name of chloroform at all.

Postscript.—Since writing the above, my attention has been called to a paper by Dr. Wilson, on the specific gravity of chloroform, which he was not able to obtain higher than 1·498. I have therefore to add, that every specimen, whether of specific gravity 1·480, 1·490 or 1·497, which I purified as above, acquired the same density of 1·500, as ascertained by the use of a very delicate and accurate bead (made by Lovi), which sank at 60°·5 and rose at 59°·5; and also by three successive weighings with a very delicate balance. It will also be seen, that three commercial specimens had this density; I could detect no foreign matter in my chloroform; and besides, every foreign matter that is likely to occur *lowers* the density. I have no doubt that Dr. Wilson's specimens would have coloured the acid and left a smell on the hand.

I may add, for the maker, that, after distilling the materials which yield chloroform, no distillation or rectification is needed. He has only to wash the heavy fluid with water till its volume no longer diminishes, and then to use the oil of vitriol as above, finishing with the oxide of manganese. Distillation with the acid is of no use, because no proper contact can take place, the chloroform distilling from the surface as it would from mercury. In testing by oil of vitriol, it is best to use some ounces of chloroform, and to shake it in a phial, because in a test-tube, the colour produced, if not strong, may be overlooked.

* Dr. Simpson informs me, that the purest chloroform he has used not unfrequently causes vomiting. On further inquiries, I find that this occurs when it is administered after a full meal. This can easily be avoided, and must not be confounded with the headache, nausea and vomiting alluded to in sections 4 and 5, which symptoms are persistent, and occurred in my experiments always with an empty stomach, the experiments being made an hour or two before dinner. Mr. Carmichael, assistant to Dr. Simpson, has mentioned to me some facts which confirm the view I have taken. At one period, for more than a week, Dr. Simpson and Mr. Carmichael were kept in a state of continual anxiety by the occurrence, in all the puerperal cases in which chloroform was used, of very unpleasant symptoms, particularly of frequent pulse and other febrile symptoms, lasting for some days. At last, after much annoyance from this cause, it occurred to Dr. Simpson that he was using one particular specimen of chloroform, above the average in quality. As soon as this idea occurred, he threw away all that remained, and returned to that which he had generally used. The unpleasant symptoms no longer appeared. [I regret much that I had not an opportunity of examining that specimen; but I may add, that the maker, not an Edinburgh one, now produces chloroform of much better quality, though not yet absolutely pure.] But the striking fact is this, that Dr. Simpson and Mr. Carmichael state, *that during the period above alluded to, when that one kind of chloroform alone was used by them, their handkerchiefs became quite offensive from the smell left on them, which even adhered to them after washing.* There can, I think, be no doubt, that here the oily impurities alluded to in sections 4 and 5 were present in notable quantity.

While I acquit the makers of chloroform who have sold an impure drug of all desire or intention to adulterate it, I feel it my duty to point out, that the system which permits *any one* to set up as a manufacturer of this or of any other potent remedy, without let or hindrance, without any test of his qualifications, without, in short, enforcing a knowledge of chemistry and pharmacy as an essential condition, is a radically bad one; and that our law, in relation to druggists and apothecaries, requires reformation. In fact, the evils naturally resulting from it are only neutralized, and that but in part, by the good feeling and principle of the leading manufacturers.

To illustrate this, I may remark, that some of the makers of chloroform must have been very ignorant even of what was known and published concerning its properties; for among the specimens I examined are several of specific gravity below 1·480, which was long ago given as the standard, even so low as 1·347.

That this neglect proceeded more from ignorance than from intention, is, I think, plain from the fact, that a specimen labeled "Pure Chloroform" actually contained only a trace, about one-thirtieth, of that substance. I did not ascertain its specific gravity, which must have been far lower than 1·200 or 1·100, nay, possibly under 1·000, because its impurity was so obvious in every other respect, and the quantity I had was too small; but on examining it further, I am convinced that its origin was this:—The maker, after distilling the materials, obtained of course two liquids, a lighter and a heavier. He evidently *did not know* that the latter was the chloroform, and therefore threw it away, and preserved the *lighter*—a mixture of pyroxilic spirit, of its natural impurities, of the deleterious chlorinated oils and *a trace* of chloroform. At least, such are its characters; and it exactly resembles what would be obtained in the way supposed. But what a fearful degree of ignorance (without any evil intention) is here exhibited! And yet this maker was free to produce and sell *pure chloroform*, which was actually almost *pure from chloroform* and loaded with deleterious agents.—*Monthly Journal of Medical Science*, May 1850.

On some new Salts of Nicotine. By J. Bödeker, Jun.

The following salts of nicotine were prepared on the occasion of making some experiments to procure pure from impure brown-coloured nicotine. The property which nicotine possesses of furnishing a beautiful crystalline compound with perchloride of mercury proved exceedingly useful for the attainment of this object.

1. *Nicotine and Perchloride of Mercury*, $Nic + 3HgCl$.—This compound forms transparent, colourless or pale yellowish crystals, which are sometimes obtained an inch in length; it is but little soluble in cold water and alcohol, and is decomposed by hot, in which it melts, and is converted into a brown resinous body. It dissolves more readily and without decomposition in acidulated water.

It is procured by mixing a saturated solution of perchloride of mercury with a solution of nicotine in dilute muriatic acid until the precipitate produced will no longer dissolve. After standing several days, the salt separates from the slightly turbid solution in crystals.

If the solution of nicotine is too concentrated, an oily body separates after some time, which is insoluble in water, but dissolves easily in dilute muriatic acid, and may be converted by more perchloride of mercury into the crystalline salt.

To determine the amount of chlorine, 1·0 grm. of the salt was dissolved in very dilute hot nitric acid, precipitated with nitrate of silver and the chloride of silver fused; its weight amounted to 0·875 grm. =21·6 per cent. chlorine. The mercury was estimated by precipitating the solution of 1·0 grm. of the salt in very dilute nitric acid with a current of sulphuretted hydrogen, when 0·718 grm. of sulphuret of mercury (dried at 212°) was obtained =61·9 per cent. of mercury. The formula given above requires 21·71 chlorine and 61·4 mercury. This compound is consequently distinct from that which Ortigosa obtained by precipitating perchloride of mercury with free nicotine, and which is $\overset{+}{\text{Nic}}=\text{HgCl}$.

2. *Periodide of Nicotine and Mercury*, $\overset{+}{\text{Nic}}\text{HI}+\text{HgI}$.—It forms small yellowish prisms, and is only sparingly soluble in cold water and alcohol, whilst in hot it is decomposed with separation of a reddish-yellow resinous mass, which is insoluble even in solution of caustic potash. This salt is formed when nicotine is dissolved in dilute hydriodic acid, and a saturated solution of periodide of mercury in hydriodic acid is added to it until the precipitate produced begins to be permanent, and the liquid remains turbid. After a time the salt crystallizes out. The mother-liquor cannot be concentrated by evaporation without decomposition. The salt was analysed in the same way as the previous one, and furnished 22·71 per cent. mercury and 58·33 iodine. Consequently this salt has not an analogous composition to the preceding one, but contains hydiodate of nicotine combined with periodide of mercury.

3. *Nicotine, Perchloride and Percyanide of Mercury.*—This compound crystallizes in colourless bundles of silky prisms, and dissolves easily and without decomposition in cold and hot water and alcohol. The solution is not precipitated either cold or hot by solution of caustic potash; but if caustic potash is poured over the crystals, they turn reddish yellow, as if peroxide of mercury were separated; with muriatic acid they disengage prussic acid.

This compound is obtained when an equal bulk of a saturated solution of percyanide of mercury is added to a neutral solution of nicotine in dilute muriatic acid. If the mixture is too dilute, it cannot be concentrated by evaporation without decomposition. The composition of this salt is still left in doubt. Only one analysis of it was made, in which the author obtained 60·85 per cent. mercury, 17·76 chlorine, and 2·46 per cent. of cyanogen, according to which it appears to be $2\overset{+}{\text{Nic}}+5\text{HgCl}+\text{HgCy}$. It might however perhaps

prove, on a more careful analysis, to be $\dot{N}ic + 2HgCl + HgCy$, *i. e.* the nicotine and perchloride of mercury first described, in which 1 HgCl is replaced by 1 HgCy.—Liebig's *Annalen*, March 1850.

Researches on Chromium. *By* J. Lefort.

On the Equivalent of Chromium.—Chemists are not yet agreed as to the equivalent of chromium. Without attempting to notice more particularly all the salts which have been employed for this determination by my predecessors, I may nevertheless state that none appear to me to furnish results so certain as the chromate of baryta. This salt can always be obtained in a perfectly neutral state, and may be exposed to a tolerably high temperature without being even partially decomposed. The chromate of baryta was weighed off, and then treated with hot nitric acid, in which it dissolved without residue. Sulphuric acid, poured in slight excess into the liquid, forms sulphate of baryta, which merely requires to be washed several times with boiling water to obtain it perfectly white. The mean of ten analyses, which agree very closely, is 60·10 of baryta to 100 of chromium. Calculating the equivalent of chromium upon these data, we find the number 333·50, which has been used in the following analyses.

Hydrates of the Sesquioxide of Chromium.—It is known that the salts of the sesquioxide of chromium may exist in three different modifications; they may be green, violet-blue and red. These isomeric conditions have formed the subject of some very interesting investigations, but the conclusions arrived at differ; some chemists have enounced the opinion that the changes of colour arose from a loss of water, which the salts experience when submitted to the action of heat; others, and at their head the illustrious Berzelius, consider that under the influence of heat the oxide of chromium undergoes an alteration in the grouping of the atoms constituting its molecule.

When the action which the alkalies exert upon the salts of chromium is examined more closely, some very marked differences are observed according as the experiment is made with potash or ammonia.

Whenever a green, violet-blue or red salt of chromium is treated with a solution of potash or soda, solution is soon effected if the alkali is in excess. It is green with the green and violet-blue salts; and violet-blue, then green, with those of the red modification. These solutions, left to themselves or heated, deposit two hydrates of the sesquioxide of different composition, although belonging to the green modification.

I. The first of these hydrates is only obtained by leaving a solution of chromite of potash to itself. The affinity uniting the acid and base being very feeble, the oxide is deposited in the gelatinous state of a very beautiful green colour. It contracts in drying into very hard black fragments. To remove the whole of the interstitial

water, it must be reduced to a very fine powder, and left over sulphuric acid until it experiences no further loss in weight; it then forms a dark green powder. On analysis it furnished the following results:—

Chromium	..	2 =	667·00	58·91
Oxygen..... ..	..	3	300·00	
Water	41·22	41·76	6	675·00	41·09

This hydrate begins to part with water at about 167° F.

II. The second hydrate is obtained whenever a green, violet-blue or red salt of chromium is poured into a boiling solution of caustic potash, or a solution of chromite of potash is heated. The resulting oxide possesses all the physical characters of the preceding one, but it contains 1 equiv. less water, and it does not part with this below 176°. I obtained the following numbers on analysis:—

Chromium	..	2 =	667·0	63·23
Oxygen	..	3	300·0	
Water.....	36·81	36·44	5	562·5	36·77

These two hydrates are certainly the same as those previously analysed by M. Fremy, and for which he found 9 and 8 equivs. of water. But that chemist employed a current of dry air to remove their water, and I am inclined to think that these oxides were not deprived of all their interstitial water by that method. I submitted all the hydrates described in this paper to a current of very dry air until they lost no more in weight; with all I obtained the same results as when they were exposed in a closed atmosphere above caustic lime and concentrated sulphuric acid.

III. The preparation of the hydrate of the violet-blue modification is more difficult. It is necessary to use the red modification, and we shall therefore first treat of this hydrate.

When a solution of a green or violet-blue salt of chromium is poured into caustic ammonia, the hydrate which falls is observed after some time to assume a red tint, and at the same time the supernatant liquid becomes of a wine-red colour. M. Lœwel, who first observed this reaction, correctly conceived that the oxide existed in it in a new isomeric state. To obtain this modification of the hydrate, some of the green hydrate may be left for several days in the presence of ammonia; but the change is long taking place, and the product is never absolutely pure. The following is the method which I have found to succeed best:—

On pouring a concentrated solution of violet chrome-alum into an excess of ammonia, the oxide which falls soon acquires a red colour, and then dissolves in the free ammonia. If this solution is left exposed to the air or placed over sulphuric acid, at the same time that the alkali is disengaged, a violet powder is precipitated. The whole of the oxide of chromium may be precipitated in this manner, and the liquid only contain the double sulphate of potash and ammonia. The hydrate of the red modification is a very light powder; dissolved in acids, it furnishes red salts, which, by concentration in a dry atmosphere, return to the violet-blue modification. It begins to

lose water already at 167°; at 248° the loss is complete, but at the same time it passes into the violet-blue, and then green modification. It gave on analysis—

Chromium			2 = 667·0	48·86
Oxygen			3 = 300·0	
Water	51·73	51·20	9	1012·5	51·14

IV. I have stated above, that, to obtain the hydrate of the violet-blue oxide of chromium, it was requisite to employ the oxide of the red modification. For this purpose an amaranth solution of chrome alum in ammonia is heated in the water-bath to a temperature not exceeding 131°. As the ammonia escapes, a greenish-gray powder is deposited, which is the hydrate of the violet-blue modification; it begins to part with water at 167°. When it lost no more water over sulphuric acid, it was analysed, and gave the following numbers:—

Chromium			2 = 667·0	55·12
Oxygen			3 = 300·0	
Water	44·62	44·21	7	787·5	44·88

To conclude, the oxides of chromium of the green, violet-blue and red modifications form four well-defined hydrates, which may be represented as follows:—

Cr^2O^3+5HO Cr^2O^3+7HO
Cr^2O^3+6HO Cr^2O^3+9HO.

These oxides furnish with acids salts corresponding to their modifications; but, as was well observed by M. Lœwel, all of them return with time, by some molecular change, to the violet-blue modification, which appears to be the normal state of the oxide in these different compounds.—*Comptes Rendus*, April 8, 1850.

On the Formula of the Basic Kinate of Copper.
By P. Kremers.

Various discrepancies occur in the analytical results of kinic acid and the kinates. Several years ago Liebig examined the crystallized kinic acid, and likewise the basic kinate of copper, and gave the formula $C^{14}H^{12}O^{12}$ for the acid. The basic kinate of copper lost at 248° F., 12·83 per cent. of water =4 atoms. It further contained 27·63 per cent. oxide of copper. Woskresensky adopted the same formula for kinic acid, but calculated from his analysis of the basic kinate of copper 1 atom more water. Baup assigned the formula $C^{15}H^{10}O^{10}$ to the anhydrous kinic acid, and to the basic kinate of copper the formula $2CuO, C^{15}H^{15}O^{15}$. He also obtained 27·586 per cent. oxide of copper, but found rather more water of crystallization, viz. 14·48 per cent.

The salt analysed by the author was prepared in the following manner:—Kinate of lime was decomposed with a slight excess of oxalic acid, the filtered solution saturated with carbonate of baryta, and separated from the oxalate of baryta. The solution of the kinate of baryta was now mixed with sulphate of copper, taking care

to use an excess of the baryta salt. The solution of the neutral kinate of copper, filtered from the sulphate of baryta, was mixed with barytic water as long as the precipitate formed at first redissolved. The liquid assumed a beautiful dark green colour, and deposited, upon being kept for some time in a gently heated spot, measurable crystals of basic kinate of copper. They were purified from adherent mother-liquor, and submitted to analysis, after having been dried over sulphuric acid until they showed no further loss in weight.

This salt, heated to 248°, lost 12·85 per cent., corresponding to 4 atoms of water; it cannot be heated above 280° without decomposition. The analysis gave for the basic kinate of copper the formula $2CuO, C^{14} H^{14} O^{14}$; and from the loss in weight which it experiences at 248°, the formula $C^{14} H^{10} O^{10}$ is deducible for the anhydrous kinic acid, as we may certainly assume that this salt parts with the whole of its water at the above elevated temperature. The analysis gave—

Oxide of copper.....	27·42	2	27·45
Carbon	28·83	14	29·02
Hydrogen	4·95	14	4·84
Oxygen	38·79	14	38·69

Liebig's *Annalen*, lxxii. p. 92.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new kind of Gunpowder. By M. Augendre.

According to numerous experiments, which the author has made in order to prepare a gunpowder from the yellow prussiate of potash, the following proportions appear to be the most favourable for obtaining the greatest effect with the least residue:—

Powdered crystallized yellow prussiate of potash	1 part.
White sugar	1 part.
Chlorate of potash	2 parts.

The constituents are reduced to powder separately, and then mixed with the hand. In experiments with small quantities, for instance a few grammes, they may be pounded together in an agate mortar. Not the least fear need be entertained of the most powerful friction. In preparing larger quantities, the mixture is moistened with 2 or 3 per cent. of water, and pounded in a bronze mortar with a wooden pestle. The author however has for a long time made use of bronze mortar and pestle only. The mixture does not require to be so intimately mixed as with ordinary gunpowder; a quarter of an hour's trituration suffices for small quantities. The powder is granulated in the usual way, and dried in the air.

This powder is white. It is fired with the greatest ease, both in

the granular state as well as in the form of an impalpable powder, by contact with an incandescent or lighted body. The flame with which it burns is greater than that of ordinary powder, and it leaves less residue. As taken from the mortar it is perfectly inflammable, so that there is never any fear of its missing fire. It must be exceedingly dry for a violent blow of iron to explode it; friction between two polished bodies never produces this effect, nor does a blow of wood upon wood or wood upon metal.

This powder has the following advantages over ordinary gunpowder:—It is formed of substances whose composition is well determined and fixed, and can therefore always be obtained of the same strength by weighing off the constituents. These substances are unalterable by the action of dry or moist air, so that they can be kept any time, which cannot be done with the charcoal used for ordinary gunpowder. The manufacture requiring less time, a fortress might, in case of necessity, be provided with the several constituents in powder, and the mixture made when required, which would avoid the dangers of the present large deposits of gunpowder. The force is much greater; there is therefore space for a larger number of charges in the artillery caissons. Lastly, it has the advantage that the dust has the same effect as the grain, so that each constituent might be reduced to a very fine powder separately by ventilation, and the several powders then mixed in a rotating leather barrel.

The new powder has the following disadvantages:—It oxidizes the iron barrels very much, so that its use is limited to bronze barrels and for filling hollow projectiles. It is more easily inflamed than ordinary gunpowder, but not so readily as other mixtures with chlorate of potash.

The author directs attention to the circumstance, readily conceivable from the behaviour of the chlorate of potash towards several other substances, that the greatest care should be taken to avoid introducing into the mixture any charcoal or sulphur, or mixing any ordinary gunpowder with this powder. The author describes an accident which occurred to him from this cause. He triturated some powder which had been kept in a powder-flask, and had become mixed with a few granules of ordinary gunpowder; a further quantity of the prussiate powder was added to it, so that the whole amounted to somewhat more than 50 grms.; on the second or third turn of the pestle, the whole mass exploded with a noise like the report of a cannon. The mortar remained entire, but the author lost eyebrows and eyelashes, and remained for two days uncertain whether he should not lose his sight, as the eyes were unable to support the light.—*Comptes Rendus,* xxx. p. 179.

Red Colour for Paper-Hangings, &c.

It is proposed to employ the red chloride of chromium for the production of an intense red-violet colour, possessing metallic lustre, proper for printing or staining paper.

This product is prepared, as is well known, by passing a current of dry chlorine gas over a mixture of powdered charcoal and calcined oxide of chromium, enclosed in a glass tube. Attention must be especially given in this operation to the fact, that by reason of the difficulty of volatilization of the product the chloride prepared by a first operation remains mixed with the powdered charcoal. It is therefore requisite to submit this mixture of charcoal and chloride of chromium to a second operation, taking care to cover the bottom only of the glass tube with it, in which case the product will be sublimed in the upper part of the tube. The heat of an Argand lamp, the flame of which is brought gradually upon the tube, will suffice for the formation of the chloride, which soon appears in the form of brilliant micaceous peach-coloured spangles. The chloride is then ground in a mortar, and thickened with a mucilage of gum. On being laid upon paper, it will display its original colour, and will resist the action not only of acids and alkalies, but also the direct action of the solar rays.—Newton's *Journal*, April 1860.

PATENT.

Patent granted to James Robinson *for Improvements in Manufacturing Orchil and Cudbear.*

In the manufacture of orchil and cudbear, it is the practice to make the ground lichens into a paste with liquid ammonia, and then to submit that paste to the action of the atmosphere; but in consequence of the mixture being in a thick mass, a considerable length of time is occupied in turning it over and over, in order that the whole of it may be subjected to the action of the atmosphere; and the manufacture of it is therefore attended with considerable difficulty and expense.

The first part of this invention consists in causing the paste, prepared in the ordinary manner, to be forced through small openings or orifices, of any required form, into vessels or receivers, whereby the air will be enabled to act upon the paste with greater effect, and the time occupied in the manufacture will therefore be considerably shortened. For obtaining paste-orchil, the paste is to be subdivided in this manner twice a day, and this process should be continued for three days.

The second part of the invention consists in a mode of drying paste-orchil for the purpose of converting it into cudbear. The patentee takes orchil-paste which has been subdivided in the manner above described, or orchil-paste prepared in the ordinary way, and passes it through a machine of a similar character to that above mentioned, permitting it to fall lightly on to a suitable surface, for the purpose of drying; when dry it will be fit to be ground as usual. —Sealed August 30, 1849.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Stibæthyle. *By* C. Löwig *and* E. Schweitzer.

The authors have applied the name of *stibæthyle* to an organic radical containing antimony and æther; it is formed by the action of chloride, bromide or iodide of æthyle upon an alloy of antimony and potassium.

This alloy of antimony and potassium was prepared by heating to redness an intimate mixture of 3 parts crude cream of tartar with 4 parts of antimony. The mixture is heated in a covered crucible, at first slowly until the cream of tartar is carbonized, and then exposed for an hour to a white heat, the furnace closed air-tight, and the crucible left to cool slowly, for which it requires at least twenty-four hours. In this manner a perfectly crystalline regulus, of a brilliant metallic lustre, is obtained, which decomposes water with violent evolution of hydrogen, oxidizes but slowly in the air owing to its density, and may be reduced quickly to a fine powder in a dry mortar; it becomes heated however in this operation, and very soon burns in the air. This may be prevented by mixing 2 to 3 parts of fine quartz sand with it on pulverization. According to an analysis of Hilgard, this alloy contains 12 per cent. of potassium.

For the preparation of stibæthyle, the iodide of æthyle is best adapted, because it is more readily decomposed than the bromide of æthyle; in like manner nitrate of silver is immediately precipitated by an alcoholic solution of iodide of æthyle, whilst bromide of æthyle is only acted upon after some time. The iodide of æthyle is obtained according to the usual method, by the mutual action of iodine and phosphorus upon alcohol. It is requisite, in order to obtain it perfectly free from phosphorus and water, to treat it several times with iodine and chloride of calcium. When the finely powdered alloy is mixed with iodide of æthyle, an exceedingly violent reaction sets in after a few minutes, which, when the quantity of the substances operated upon is sufficiently large, may cause the mixture to take fire. It is impossible to operate with large quantities, and it is also requisite, in order to moderate the violence of the action, to mix the alloy with 2 to 3 parts of finely powdered quartz. The alloy of antimony and potassium must be used in large excess in proportion to the iodide of æthyle, because, as will be seen from the

analyses, 3 atoms of iodine are replaced by 1 atom of antimony, and the alloy contains only 12 per cent. of potassium.

The authors find it most advantageous to employ, for the preparation of stibæthyle, small flasks with short necks of from 3 to 4 ounces capacity. They are two-thirds filled with the recently powdered mixture of the alloy and sand, and the iodide of æthyle immediately added in the proportion above stated. The flask is connected with an ordinary glass distillation-tube, which terminates in a small receiver; after a few minutes the reaction commences; the heat evolved volatilizes the excess of iodide of æthyle, and the flask itself becomes filled with gaseous iodide of æthyle. As soon as no more iodide of æthyle passes over, the tube is removed, and the flask, while still warm, connected as quickly as possible with the suitable apparatus. This consists of the following arrangement:—A tall, broad glass cylinder is closed with a cork having three perforations; through one aperture a glass tube passes, reaching to the bottom, and which externally is bent at a right angle, and connected with an apparatus, in which during the operation carbonic acid is constantly disengaged, and passed through a long chloride of calcium tube. A glass tube, from 1 foot to 2 feet in length, is inserted in the second aperture, and terminates just below the cork, through which the carbonic acid escapes. Through the third very narrow aperture is passed the distillation-tube nearly to the bottom of the vessel, in which a small flask, partially filled with the alloy of antimony and potassium, has been previously placed for the reception of the product, and to be employed afterwards for its distillation. Before commencing the operation, a rapid current of carbonic acid is passed through the apparatus for at least half an hour, in order to fill every part of the apparatus with carbonic acid. The flask is now heated over a spirit-lamp, at first gently, but gradually increasing in strength until no more drops pass over. The flask is then removed, the distillation-tube closed with wax without taking it out of the apparatus; and the operation, which requires twenty minutes at the utmost, begun with a second flask. When two persons work together, and have from twenty to twenty-four flasks in readiness, it is easy to procure from 4 to 5 oz. of the crude product in a day. The flask in which the distillate was collected is now closed in the atmosphere of carbonic acid. After some hours the product is rectified in the same apparatus. In order to ascertain whether, in the action of the iodide of æthyle upon the alloy of antimony and potassium, different products were formed, several small flasks were placed in the apparatus, and what passed over collected in four portions, which can easily be effected, and without loss, by turning the cylindrical vessel. Although stibæthyle does not possess an agreeable odour, it is so little oppressive that it can be experimented with in a room. The results of the analyses of the different portions obtained in the rectification are given further on. To weigh off the substance, small, narrow cylindrical tubes were used, which were drawn out into a long point. At the place where the capillary tube begins, they were bent at an acute angle; the capillary tube was so

long, that it reached nearly to the bottom of the above-mentioned glass cylinder, filled with carbonic acid, into which it was passed through the aperture in which during the distillation the distillation-tube was inserted; the little cylindrical tubes themselves were outside the apparatus; they were heated as strongly as possible over a spirit-lamp without rendering the glass soft. After cooling, they were again heated, and this repeated nine or ten times, when they were perfectly filled with carbonic acid. The point was now dipped into the substance, and filled so far with it that about the sixth part remained empty, and no more liquid was contained in the capillary tube. Before removing the point from the apparatus, it was left in the atmosphere of carbonic acid until the small quantity of substance adhering to it had evaporated; the point was then sealed before the blowpipe. In order to bring the cylinder into the combustion-tube, it was cut with a file at the curve, and the point broken off as the cylinder was placed in the combustion-tube; no fumes were given off, the cylinder being full of carbonic acid. The capillary tube was then broken in two or three places, and likewise placed in the combustion-tube.

The combustion with oxide of copper proceeds without difficulty, but the oxidation is imperfect. From the same substance, 25, 28, 30, and even 33 per cent. of carbon were obtained. The cause is owing to the decomposibility of the compound by heat; an intimate mixture (perhaps a combination) of antimony and carbon separates, upon which the oxide of copper has no further action. The combustion however is perfectly successful when from 4 to 5 per cent. of chlorate of potash is mixed with the oxide of copper. The chlorate of potash is fused, then reduced to powder, mixed with the still warm oxide of copper, and the mixture left for some days over sulphuric acid under a bell-glass. This mixture yields a uniform disengagement of oxygen, and the operation is easily regulated. Some pure oxide of copper is first placed in the combustion-tube, then a layer of the mixture, after which the substance, then the mixture, so as to fill half the tube, and lastly pure oxide of copper.

Neither nitric acid nor *aqua regia* effects the perfect oxidation of the antimony. It was sought to determine its amount by bringing oxide of zinc, with which some chlorate of potash had been mixed, into the combustion-tube; differences amounting to 5 per cent. were obtained according to the temperature employed for the combustion. At very high temperatures a combination of oxide of antimony with oxide of zinc appears to be formed, which is not acted upon either by muriatic acid or *aqua regia*. Better and more accordant results are obtained when no chlorate of potash is added to the oxide of zinc. The antimony then separates in the metallic state, and is easily dissolved by nitromuriatic acid. The most trustworthy results were obtained by passing the compound through red-hot powdered quartz. A long combustion-tube was employed, the lower portion filled with some sand, then the substance, and the remainder with quartz sand for three-fourths, and the empty portion of the tube allowed to project out of the combustion-furnace so as to re-

main cold, in order that any antimony which might possibly be volatilized might be condensed. The quartz sand was heated by degrees to redness, as in organic analyses, and then the vapour of the compound passed over it. As soon as it came in contact with the red-hot sand, the antimony separated in a crystalline state, and the whole of it was generally found together in a very small space. When cold, the contents of the tube were emptied into a beaker, the tube rinsed with nitromuriatic acid, and the sand digested for several hours with fuming *aqua regia*. The filtered liquid was diluted with a solution of tartaric acid, the antimony precipitated by sulphuretted hydrogen, and the quantity of the antimony found by estimating the amount of sulphur in the perfectly dried sulphuret of antimony.

In the first portion some colourless acicular crystals formed after some time, which contained iodine; on pouring dilute nitric acid over them, iodine was set free, which is not the case with iodide of æthyle. These crystals however were obtained in such small quantity, that it was not possible to make a more complete examination of them. The liquid portion also contains iodine, which is immediately eliminated on the addition of concentrated nitric acid. In the analysis of the liquid portion with oxide of copper and chlorate of potash, towards the end of the operation some iodine suddenly separated in the tube of the chloride of calcium apparatus. Without doubt some iodide of copper was first formed, which at last, after all had been oxidized, was decomposed by the eliminated oxygen into iodine and oxide of copper. The second, third, and fourth portions, however, were perfectly free from iodine.

The following are the results of some analyses of the second, third and fourth portions of the distillate. They agree best with the formula $C^{12} H^{15} Sb$:—

	2nd portion.		3rd portion.	4th portion.					
C	32·74	32·88	34·27	33·52	34·47		12	72·0	33·32
H	7·18	6·99	7·26	7·24	7·28	7·19	15	15·0	6·94
Sb	59·82	59·42	60·22	58·79	..	..	1	129·2	59·74
								216·2	100·00

There are consequently 3 atoms of æthyle to 1 of antimony $= Ae^3 Sb$. Stibæthyle is therefore insofar equivalent with antimoniuretted hydrogen, as in the former 3 atoms of hydrogen are replaced by 3 atoms of æthyle; its composition consequently presents nothing remarkable.

Stibæthyle is a limpid, extremely mobile liquid, of pretty strong refracting power, with a disagreeable alliaceous odour, which however soon disappears; it does not solidify at −20° F. When a glass rod is dipped in it, and then held in the air, dense white fumes are formed; and after a few moments it takes fire, and burns with a dazzling white, highly luminous flame. It is heavier than water, and insoluble in it, but dissolves readily in alcohol and in æther. When stibæthyle is passed through a fine aperture into pure oxygen,

it burns with a most brilliant light. Fuming nitric acid likewise produces a magnificent combustion. It unites with bromine with detonation. When stibæthyle is conveyed into a balloon, taking care that it does not ignite, a white vapour is formed, which is deposited on the sides of the vessel in the state of a powder; at the same time there is formed, especially when a large quantity is allowed to oxidize in this manner, a tenacious, colourless, transparent mass, which dissolves in æther, whilst the pulverulent body is insoluble in it; æther may therefore be employed for separating the two substances. When an alcoholic solution of stibæthyle is left t evaporate slowly in a loosely covered vessel, it leaves a tenacious mass, which can easily be separated by æther into the two substances just mentioned. The portion soluble in æther is left on evaporation in the form of a tenacious, colourless syrup, which gradually dries on the water-bath to a transparent mass. The pulverulent substance, insoluble in æther, dissolves readily in water and alcohol. The solutions have a distinct acid reaction, and eliminate carbonic acid from its compounds. This body possesses a strongly bitter taste, very similar to that of the sulphate of quinine. The aqueous, as well as the alcoholic solution, which are both easily filtered, possess the remarkable property of becoming thick like starch paste on being heated, and finally dry to a porcelaneous very friable mass. The dry residue dissolves again easily in cold water and alcohol, and the solutions exhibit the same phænomenon on the application of heat. The aqueous solution of this substance, which the authors have preliminarily named *stibæthylic acid*, furnishes with sulphuretted hydrogen a light yellow precipitate, which possesses an extremely disagreeable, persistent, mercaptan-like odour, and dissolves readily both in potash and sulphuret of potassium. When the aqueous solution of stibæthylic acid is accurately saturated with potash, and then with sulphuretted hydrogen, an extremely soluble sulphosalt is obtained, which possesses a great tendency to crystallize. When the precipitate with sulphuretted hydrogen is dried over sulphuric acid under a bell-glass, it forms a very beautiful bright yellow powder; in the water-bath it changes its colour, and turns brown like kermes. Fuming nitric acid decomposes the substance with flame; on heating it over the spirit-lamp, a liquid product distils over, which has all the properties of the sulphuret of æthyle, and the residue consists of sulphuret of antimony.

When the aqueous solution of stibæthylic acid is mixed with concentrated muriatic acid, a yellowish heavy oily liquid immediately separates. It is soluble in pure water; but on adding strong muriatic acid to the solution, the oily substance is immediately reobtained.

The syrupy mass which is left on the evaporation of the ætherial solution, and which is simultaneously formed with the stibæthylic acid on spontaneous oxidation, is scarcely soluble in water, but easily dissolves, as already stated, in æther and in alcohol. It likewise readily dissolves in an aqueous solution of potash. If the alcoholic solution is digested for some time, and then slightly super-

saturated with dilute sulphuric acid, a white precipitate is deposited, which immediately forms with concentrated muriatic acid a liquid chlorinated compound, which sinks in the water.

Cold dilute nitric acid exhibits no action upon stibæthyle, but on the application of heat complete solution results, with a slight disengagement of nitrous acid; when this is evaporated at a gentle heat, very beautiful, colourless, transparent crystals are obtained, which are scarcely soluble in water containing nitric acid, but dissolve very readily in pure water. From the aqueous solution the compound crystallizes in remarkably beautiful, large, rhomboidal crystals, which possess a bitter taste, exert a slightly acid reaction upon litmus, and melt between 104° and 122° F. to a heavy colourless liquid, which on cooling solidifies to a transparent crystalline mass. On pouring a little water over it, it turns white, and after some time the same crystals are obtained. This compound is a salt of nitric acid; sulphuric acid eliminates nitric acid from it, and on adding to one of the crystals some protosulphate of iron, water and sulphuric acid, the well-known reaction of nitric acid is obtained.

It results from the preceding that stibæthyle possesses all the properties of a radical, and may be placed by the side of kakodyle. The authors intend making further researches on this class of compounds, and promise to communicate soon the results they have obtained on similar compounds of methyle, amyle, &c.—*Mitth. d. Zurch. Naturforsch. Gesellschaft*, No. xlv. pp. 1–16.

On the Behaviour of Arsenic, Antimony and Tin towards Chloride of Sulphur. *By* Prof. F. Wöhler.

It does not appear to be known that the chloride of sulphur, the ordinary protochloride S^2 Cl, is completely decomposed with great violence by arsenic, antimony and tin. The following experiments on this subject were made by M. Stümcke.

When chloride of sulphur is poured over coarsely pounded *arsenic* contained in a tubulated retort, after a few minutes so much heat is evolved that the mixture begins to boil, and a great portion of the chloride of sulphur distils over unaltered. If it be poured back over the residue containing the excess of arsenic, and the action completed with the assistance of heat, the whole of the chloride of sulphur is decomposed, and colourless, perfectly pure protochloride of arsenic distils over. The whole of the sulphur of the chloride of sulphur remains in the retort with the excess of arsenic employed.

Orpiment and *realgar*, even in the fused state, decompose the chloride of sulphur just as easily with evolution of heat, and distil over as protochloride of arsenic.

Antimony behaves in the same manner towards chloride of sulphur; it becomes spontaneously heated to boiling; perchloride of antimony distils over, which is partially converted into protochloride. The *black sulphuret of antimony* exhibits the same behaviour.

Tin, in the state of filings, acts most violently upon the chloride of sulphur. Owing to the intense heat evolved, a portion of the

chloride of sulphur distils over unaltered, and should be again poured over the tin. Pure perchloride of tin then distils over. Chloride of sulphur does not decompose the *persulphuret of tin*.

It acts but slightly and slowly upon zinc, iron, nickel and copper. —Liebig's *Annalen*, March 1850.

On a new kind of Sugar obtained from Flesh. *By* Prof. SCHERER.

When the whole of the baryta has been precipitated by the addition of dilute sulphuric acid to the kreatine mother-liquor, according to the plan recently described by me, and the filtered liquid has been subjected to distillation in order to obtain the volatile acids, it is possible to separate from the residue of the distillation the last traces of the volatile acids, as well as the whole of the free lactic acid, by repeated agitation with æther. If the æther charged with the acids is shaken with an alkaline solution (I employ a solution of caustic soda), the same æther may be repeatedly used. When the free acids have been removed according to this method, and so much strong alcohol is gradually added to the residual liquid that it becomes turbid, and it is then set aside, nearly the whole of the potash gradually crystallizes out in combination with sulphuric acid. If fresh quantities of alcohol are constantly added, very soon crystals of a different form, and bearing great resemblance to those of native gypsum, make their appearance along with the crystals of sulphate of potash. If, finally, the mother-liquor is decanted from these mixed crystals, and they are laid upon folds of blotting-paper, the two kinds of crystals may be pretty easily separated from one another. They may be also separated by treatment with a little warm water, which removes the more readily-soluble gypsum-like crystals. The filtered solution furnishes this body on cooling in remarkably beautiful crystals, which are nearly pure, and the mother-liquor furnishes further quantities nearly to the last drop. It is easily ascertained to be of organic nature by heating it upon platinum foil; and if it has once been recrystallized by solution in as little warm water as possible, it burns pretty readily without leaving any residue. The crystals, which are mostly grouped in cauliflower-like heads, but are sometimes isolated, and are then from 3 to 4 lines long, belong to the klinorhombic system. In the dry air of a room the crystals soon become dull, opake and white, from loss of water of crystallization. This takes place more readily under the air-pump over sulphuric acid, when they part with the whole of their water of crystallization, amounting to 16·6–17 per cent.; this is also the case in the water-bath at 212°. After desiccation in the water-bath, they may be heated to 410° F. without experiencing any further loss in weight or the least change, but above 410° they begin to melt to a clear liquid. If the fused mass is quickly cooled, it crystallizes in acicular crystals, whilst on slow cooling it forms a horny amorphous mass. In both cases there is not the least loss in weight, and when dissolved in water it crystallizes without change in the original form.

At a still higher temperature the fused mass begins to disengage gas. It puffs up, and the escaping vapours burn with a pale blue slightly-luminous flame. When strongly heated, the mass is carbonized, and now burns, on being set light to, with a bright flame. The carbonaceous residue may be completely burnt with great ease over a simple spirit-lamp. The crystals lost in the water-bath 16·84 per cent. of water (the mean of four experiments). No nitrogen could be detected by combustion with soda-lime, nor sulphur by fusion with nitre and caustic potash. On combustion with oxide of copper, they furnished—

Carbon.....	40·247	40·00	12 =	40·00
Hydrogen	6·672	6·72	12	6·66
Oxygen	53·081	53·28	12	53·34

a composition which entirely corresponds to that of milk-sugar, $C^{12} H^{12} O^{12}$. If, on the other hand, we calculate the two above analyses, taking into consideration the 16·84 per cent. of water lost, we obtain—

Carbon.....	33·333	33·00	12 =	33·33
Hydrogen	7·402	7·40	16	7·40
Oxygen	59·265	59·60	16	59·27

leading to the formula $C^{12} H^{16} O^{16}$, which shows that the substance in question loses 4 equivs. water at 212° F. Theory requires 16·6 per cent. water.

This new substance differs consequently from crystallized grape-sugar in composition by containing 2 equivs. more water.

The taste of this interesting substance is at once distinctly sweet. It is readily soluble in water, sparingly in strong spirit, insoluble in absolute alcohol and æther. From the boiling spirituous solution nearly the whole separates on cooling in minute, shining, nacreous laminæ, resembling cholesterine. It is not in the least altered by evaporation to dryness with muriatic acid, nor on ebullition with dilute sulphuric acid; strong sulphuric acid colours it brownish on evaporation on the sand-bath; dilute caustic potash or caustic baryta produces no change when boiled with it; if the baryta be removed by carbonic acid or the potash by sulphuric acid, unaltered crystals of the substance are obtained. Highly concentrated caustic potash produces no change of colour on ebullition, as is the case with other sugars, and especially with grape-sugar. Sulphate of copper and potash furnish in the solution of the crystals a bluish-green precipitate, which quickly redissolves in excess of potash. Neither in the cold nor on boiling does any reduction and production of protoxide of copper take place. After standing for several days, a light blue precipitate separates from the liquid. Pettenkofer's test with pure bile and sulphuric acid did not furnish the characteristic violet colour, but only a dirty red one.

The small quantity of the substance at my disposal did not admit of my making experiments on an extensive scale to decide whether this body is susceptible of fermentation, and what kind of fermenta-

tion. Some preliminary experiments, made upon a small scale, gave the following results:—

1. A quantity of about 0·180 grm., exposed with yeast and water to the proper temperature, exhibited, even after eight days' standing, no appearance of fermentation. No carbonic acid was disengaged through the tube into the lime-water; and when, after this interval, the liquid was poured off the yeast and subjected to careful distillation, not a trace of alcohol could be detected in the distillate. On evaporating the residue of the retort, nearly the whole amount of sugar crystallized unaltered.

2. About 0·100 grm., mixed with cheese, chalk and water, and kept at the proper temperature, exhibited after a short time signs of decomposition. The liquid exhibited a pretty strong reaction of dissolved lime, disengaged carbonic acid, and when, after eight days, the experiment was terminated, traces of lactic acid and a pretty considerable quantity of butyric acid were found in the liquid.

3·80 milligrms. were exposed, with a piece of flesh which had been previously rinsed in cold water, to a temperature of 95°. In twenty-four hours a pretty strong acid reaction was perceptible; it was mixed with chalk, when disengagement of carbonic acid ensued; and when, after eight days, no more gas was given off, the liquid was boiled, filtered, mixed with a solution of chloride of zinc and evaporated to crystallization. It furnished crystals of the lactate of zinc, which were readily recognized by their form under the microscope. Oxalate of ammonia also showed, in this case, a pretty considerable amount of lime previous to the addition of the chloride of zinc; and with sulphuric acid and alcohol added to the mother-liquor of the lactate of zinc, the odour of butyric æther became perceptible.

From its composition, its incapacity of undergoing vinous fermentation under the usual conditions, and its property of passing into lactic acid, the resemblance of this body with milk-sugar is very evident; it however differs essentially from it by the 4 equivs. water, as also by the property of not reducing hydrated oxide of copper and not exhibiting Pettenkofer's reaction. I propose for this substance the name of *inosite*. I am at present engaged in experiments for the purpose of ascertaining whether it is formed as an intermediate product in the lactic acid fermentation of cane-sugar.

The question might be started, whether this new body is contained as such in the flesh extract, or is produced by the action of the chemical reagents upon any of the nitrogenous constituents. The sulphuric acid might produce such an action. Although I did not add it in excess, but only in sufficient quantity to precipitate the baryta, and although the distillation of the volatile acids was effected so that some distilled water was constantly added in order to prevent the mass becoming too thick, I shall nevertheless make this the subject of further investigation, and communicate the results on some future occasion.—Liebig's *Annalen*, March 1850.

On the Decomposition of an Aqueous Solution of Sulphurous Acid by Sulphuretted Hydrogen Gas. *By* Messrs. Sobrero *and* Selmi.

Wackenroder observed*, that a new acid of sulphur, the pentathionic acid, is formed in the action of sulphuretted hydrogen upon sulphurous acid. In the production of this acid, the sulphuretted hydrogen was passed into water which had been previously saturated with sulphurous acid. The new acid was neutralized with baryta, and the baryta salt precipitated by alcohol.

The authors conveyed the two gases simultaneously and uninterruptedly for several days into a vessel filled with water. During this operation samples of the liquid were taken out from time to time, and saturated with carbonate of baryta. This solution of the baryta salt was first poured into weak alcohol to separate the sulphate of baryta, and then into strong alcohol, and the salts thus precipitated analysed. The authors found the results of the analyses to differ considerably from each other; but if pentathionic acid were the only product formed in the reaction of sulphuretted hydrogen upon sulphurous acid, these differences ought not to occur. The numbers which the authors obtained agreed sometimes with the composition of a mixture of tetrathionate and pentathionate of baryta, and sometimes they merely found the tetrathionate of Fordos and Gelis. They obtained, for instance, the following numbers:—

			Fordos and Gelis.
Baryta	38·74	38·65	38·50
Sulphur	32·83	32·68	32·25
Oxygen combined with S.	19·31	19·55	20·16
Water	9·12	9·12	9·09

Frequently, when the clear acid liquid which had been precipitated with strong alcohol had stood for some time in an imperfectly closed vessel, prismatic crystals were obtained by slow evaporation, which after drying still contained some alcohol. The relation of the sulphur to the baryta in it was as $4\frac{1}{2}$ to 1 equiv., or as 9 : 2 equivs., which corresponds with the composition of the tetrapentathionate of baryta of Ludwig. Besides these products, the authors found pentathionic, hyposulphurous and sulphuric acids, but never the acid of Langlois. The conditions under which the one or other of these acids is formed are dependent on the temperature, concentration of the liquid, and the relative quantities in which they are brought together.

The liquid in which the decomposition takes place deposits during the operation a large amount of sulphur; but it still holds a quantity in solution, which is only precipitated when it is saturated with carbonate of soda or potash. The sulphur which is first deposited in the reaction of the gases upon each other is of a beautiful yellow colour, sometimes opake, at other times transparent. When separated from the liquid, it has an acid reaction; if water is added to

* Chem. Gaz., vol. iv. p. 465.

it, it forms an emulsion, from which it is not deposited even after several months. When a little of an aqueous solution of a potash or soda salt is added to this emulsion, a precipitate of sulphur is immediately obtained; but it is remarkable, that the sulphur precipitated by a soda salt has not lost the property of diffusing itself in water; for when the liquid containing the soda salt is poured off, and the sulphur is rinsed once or twice with water, it very soon re-acquires the property of forming an emulsion with water. But if a salt of potash has been used instead of one of soda, this property of the sulphur has disappeared; when, for instance, sulphate of potash has been employed, the sulphur is doughy, viscous and elastic, like caoutchouc, and loses none of these properties by washing. This sulphur retains with great tenacity a portion of the acid from the solution of which it was precipitated. It loses its elastic condition instantly when washed with water containing a carbonate or caustic alkali. The first sulphur capable of forming an emulsion loses this property by long exposure to the air, becoming pulverulent. The second elastic sulphur loses none of its elasticity by exposure to the air. The authors have in their possession some of this elastic sulphur, which has kept unaltered for several months.

It has been mentioned above, that the acid liquid which is produced by the action of sulphuretted hydrogen upon sulphurous acid still contains a quantity of sulphur dissolved. It is easy to be convinced of this by adding a solution of a neutral salt of potash or soda. Liquids marking 17° to 18° upon the areometer became almost solid upon the addition of a small quantity of one of these salts from separated sulphur, which must previously have been perfectly dissolved in the liquid. The same differences of behaviour are exhibited by this sulphur as in that above described.—*Ann. der Chim. et de Phys.*, xxviii. p. 210.

On the Salts which are produced by the Action of Lead upon the Nitrate of Lead. By T. Bromeis.

The lead salts described in this paper were prepared by boiling in a wide flask an excess of lead turnings with a solution of nitrate of lead. The disengagement of nitric oxide gas generally begins at about 176° F., and becomes subsequently almost imperceptible. The liquid becomes at first yellow, then paler, but never perfectly colourless. Gradually a deposit is formed in the liquid of carbonate of lead and silicate of lead, the latter, produced from the glass being strongly acted upon. On cooling, especially when rapidly cooled, the salts of nitrous acid formed separate together and are difficult to isolate. The salts were analysed according to Bunsen's method, so as to determine all the constituents; and it may in future be always employed in examining metallic salts of the acids of nitrogen. The apparatus used consisted of a chloride of calcium tube, 2 feet in length, which was connected with a tube about 20 inches in length, filled with reduced copper turnings, and serving to remove the oxygen from the air. This latter tube is drawn out at

one of its ends into a point, in order to be connected with another glass tube, 10 inches in length, and likewise drawn out to a point. In the hind portion of this tube is placed the little platinum tray filled with the substance under examination, before which reduced copper is placed. This is joined to a chloride of calcium tube, which at its other extremity is connected with another glass tube, also filled with reduced copper, the object of which is to prevent the gases diffusing from the aspirator, air and aqueous vapour, from exerting an injurious influence. This apparatus requires three furnaces for the three tubes, the central one of which must be surrounded with a piece of copper foil filled with charcoal powder, in order to prevent any ash adhering to the glass. After the copper for the two glass tubes has been dried in the water-bath, the outermost one is quickly filled and connected with the aspirator; and the platinum tray, with its contents, the weight of both of which is known, is placed in the central tube, dried copper placed before it, the chloride of calcium tube weighed, as well as the entire tube thus filled (its weight amounted to between 50 and 60 grms.); the two are connected, the glass tube carefully arranged in the copper casing, and charcoal and the apparatus placed together, without however connecting the first tube filled with copper, which during the last operations has been brought to a red heat, in order to remove all hygroscopic water. When this is done, it is also connected; and by setting the aspirator in action, a very slow current of nitrogen is passed through the apparatus. As soon as we are convinced that all atmospheric air has been removed in this manner, the last tube, situated nearest to the aspirator, is heated to redness; and then the tube containing the platinum tray is melted off with the blowpipe at its thinner portion between the copper foil and caoutchouc, and this also gradually raised to a red heat, beginning with the end turned towards the aspirator. When the experiment is finished and the tubes have cooled, the apparatus is disconnected where the chloride of calcium tube joins the outermost tube; the sealed extremity is filed off, some air carefully drawn through, and the chloride of calcium tube, together with the combustion-tube and its contents, weighed, not forgetting the fragments of glass which may have separated in disconnecting the apparatus by blowpipe and file. What the glass tube weighs less is the amount of nitrogen in the substance and water taken together; as the latter is found from the increase in weight of the chloride of calcium, the amount of nitrogen is likewise known. After removal of the copper from the tube, or better after separating the hinder portion of the combustion-tube by means of the file or a piece of incandescent charcoal, the tray with the oxide of lead is weighed. The sum of the oxide of lead + the nitrogen + the water deducted from the weight of the substance employed, furnishes the quantity of oxygen which has passed to the copper.

The salts prepared by the author are upon the whole very sparingly soluble in water; the solutions are milky; the salts with most base are the most difficult of solution. They dissolve more readily

in boiling water, and easily in acetic acid; the concentrated solution in acetic acid deposits beneath a yellowish liquid a heavy oily one, which, exposed for some time to a gentle heat, turns to a gummy, highly viscous mass. Alcohol and æther precipitate the salts from their solutions in the form of a yellowish-white powder; nitrate of copper produces a light bluish-green, protonitrate of mercury a yellowish precipitate, which immediately turns dirty green, and finally becomes brownish-black. They have an alkaline reaction. These compounds do not all bear a temperature of 212° without decomposition, as stated by Peligot; on the contrary, it commences at about 185°, except in the case of the quadribasic nitrite. Concentrated sulphuric and muriatic acids act very slowly upon them in the cold, without any perceptible evolution of red vapours. The crystals of these salts belong to the rhombic system.

Bibasic Hyponitrate of Lead, $2PbO+NO^3+HO$.—The author prepared this salt according to Peligot's directions, by heating a solution of 100 parts nitrate of lead with 63 parts of lead. This is the salt which is mainly formed at first in the action of nitrate of lead upon lead; the temperature must be kept as low as possible in its preparation, as more basic salts are readily formed at a higher temperature, and contaminate this salt. The author once obtained a salt which had the composition $4(2PbO+NO^3)+2PbO+NO^3+7HO$.

The bibasic hyponitrate of lead of the author is the salt which was first described by Proust, was considered by Berzelius and Chevreul to be a nitrite, and was proved by Peligot to be hyponitrate of lead. It crystallizes in straw-coloured, shining, rectangular prisms; it is the most soluble of all the salts in water, 1 part dissolving in about 85 parts at the ordinary temperature; at 185° it is decomposed; melts at a higher temperature in its water of crystallization with tumescence; but retains its form if deprived of its water very slowly by a gradually increasing temperature in the oil-bath, when it finally becomes white, and may now, like the other compounds, be exposed to a red heat without any change of form. If the dry salt is boiled with water, it remains unaltered, but in the presence of metallic lead it is slowly decomposed. It furnished on analysis—

Nitrogen ..	4·901	4·860	4·948	4·992	1	175·06	5·04
Oxygen....	11·198	11·104	11·121	11·082	4	400·00	11·50
Oxide of lead	79·777	79·707	79·724	79·979	2	2789·28	80·23
Water	4·124	4·329	4·207	3·947	1	112·48	3·23

A Salt, $7PbO+(NO^4+NO^5)\,3HO$, probably $(4PbO+NO^4)+(3PbO+NO^5)+3HO$, was obtained by the author on keeping the solution of the nitrate of lead for several days boiling with a large excess of lead. It separated in single, well-formed, hard crystals upon a green salt, which had crystallized out at the same time, and which could easily be removed. The salt is of a light brick-red colour; the angle of the vertical prism amounts to 123°, that of the longitudinal prism to 63°. The crystals are cleavable in the direc-

tion of the horizontal surface, and somewhat less so parallel with the surface of the vertical prism. The analysis of this compound furnished—

Nitrogen	3·089	3·015	3·106	2 =	350·12	3·08
Oxygen	7·726	7·898	7·809	9	900·00	7·93
Oxide of lead	86·032	86·015	86·028	7	9762·48	86·01
Water	3·153	3·072	3·057	3	337·44	2·98

⅔ths Hyponitrate of Lead, $7PbO+2NO^4+3HO$.—This salt was first prepared by Peligot, is of an orange colour, and is also obtained when the solution of the salt $2PbO+NO^4+HO$ is boiled with lead. Its crystals are combinations of the vertical rhombic prism with the longitudinal prism. The following results confirm those already obtained by Peligot:—

Nitrogen.....	3·194	3·176	3·139	3·204	2 =	350·12	3·11
Oxygen	7·434	7·494	7·416	7·233	8	800·00	7·11
Oxide of lead..	86·433	86·392	86·434	86·434	7	9762·48	86·78
Water.....	2·939	2·938	3·011	3·129	3	337·44	3·00

A Salt, $7PbO+(NO^3+NO^4)+3HO$, probably $(3PbO+NO^3)+(4PbO+NO^4)+HO$, was obtained by the author by the same process as followed for the preparation of the preceding salt. It likewise separates in orange-coloured crystals, but they are much more brilliant and have many more surfaces. They gave on analysis—

Nitrogen	3·284	3·101	3·205	2 =	350·12	3·14
Oxygen	6·258	6·279	5·989	7	700·00	6·28
Oxide of lead	87·724	87·676	87·710	7	9762·48	87·55
Water	2·734	2·944	3·096	3	337·44	3·03

Bibasic Nitrite of Lead, $2PbO+NO^3+HO$.—This salt is obtained, but only in small quantity, when the solution of the salt $2PbO+4NO+HO$ is boiled for some time with lead. On cooling, the nitrite separates upon the crystals of the hyponitrate in tolerably long needles, which are rectangular prisms with rhombic pyramids. This salt frequently occurs as an impurity in the preparation of the orange-coloured salt. The acicular crystals are separated mechanically from those of the hyponitrate upon which they are seated. They are of a golden-yellow colour, and furnished on analysis—

Nitrogen	4·763	5·045	1 =	175·06	5·18
Oxygen.....	8·918	8·951	3	300·00	8·89
Oxide of lead ..	82·449	82·471	2	2789·28	82·60
Water	3·870	3·533	1	112·48	3·33

Tribasic Nitrite of Lead, $3PbO+NO^3$.—This salt is constantly formed when the solution of the orange-coloured salt is boiled with lead for some hours. It separates on cooling, sometimes in fiery red, sometimes in green crystals. The crystals, of whatever colour, contain no water.

Chevreul obtained a hydrated salt in flesh-coloured needles, and Berzelius an anhydrous salt in minute brick-red laminæ. The salts furnished these chemists on analysis—

	Berzelius.	Chevreul.	Calculated.
Nitrous acid	10·17	9·9	10·20
Oxide of lead	89·83	90·1	89·80

Chevreul suspected, in consequence of the presence of water found by him, that Berzelius's salt contained less base. Subsequently Peligot stated that he had likewise obtained salts of the same colour and composition, but that they were mixtures of the orange-coloured salt $7PbO+2NO^3+3HO$ and the yellow salt $2PbO+NO^3+HO$, as on treating them with an amount of water not sufficient to dissolve them, they were decomposed into these two salts.

The existence of a tribasic nitrite of lead is considered by the author to be satisfactorily confirmed by his experiments. Berzelius's salt is tribasic according to the author, whilst that analysed by Chevreul he looks upon as quadribasic. The reasons brought forward by Peligot against the existence of the first salt are inconclusive, since the solutions of these basic salts, when treated for any length of time with boiling water, are decomposed in such a manner as to produce compounds containing less base.

The analyses made by the author are I. to III. of the brick-red salt, and IV. to VI. of the dull and shining green crystals:—

	I.	II.	III.	IV.	V.	VI.		
Nitrogen ..	3·634	3·920	3·675	3·832	3·562	3·756	1	3·76
Oxygen ..	5·985	6·179	5·962	6·243	6·578	6·335	3	6·44
PbO.....	89·453	89·339	89·573	89·573	89·383	89·364	3	89·80
Water	0·928	0·562	0·790	0·352	0·477	0·545		

Quadribasic Nitrite of Lead, $4PbO+NO^3+HO$, is the final product of the action of dilute solutions of the nitrate of lead upon lead. It is probably the one already obtained by Chevreul; the properties assigned by Berzelius to this salt agree better with those of the preceding one. Peligot analysed this salt; he obtained it of a pale rose colour, Chevreul of a flesh colour, the author of both colours, and also of a greenish-brown colour. The prisms of this salt are generally in concentric groups, of a beautiful silky lustre, low specific gravity, and may be exposed to a temperature of 302° without losing any water. The author's analyses gave—

Nitrogen	2·727	2·760	1 =	175·06	2·84
Oxygen.....	4·568	4·599	3	300·00	4·87
Oxide of lead ..	90·368	90·413	4	5578·56	90·47
Water	2·337	2·228	1	112·48	1·82

The author considers the existence of the following salts to be proved:—

Nitrites.	Hyponitrates.
$PbO+NO^3+HO$	$PbO+NO^3+HO$
$2PbO+NO^3+HO$	$2PbO+NO^3+HO$
$2PbO+NO^3$	$7PbO+NO^3+3HO$
$4PbO+NO^3+HO$	$4PbO+NO^3+3HO$.

Liebig's *Annalen*, lxxii. p. 38.

Observations on Spongy Lead. By M. Bolley.

The author obtains the spongy lead very easily in the following manner. A smooth plate of zinc is coated with a thick paste of sulphate of lead and water about one inch deep. This is now placed in a vessel filled with a solution of common salt in a somewhat inclined position, and just so that the liquid entirely covers it, so that in the decomposition, the salts newly formed readily flow off to the bottom. Upon the sulphate of lead it is best to place another plate of zinc. In the course of nine or ten days the lead salt is changed into a plate of lead sponge, which is extremely well adapted for receiving impressions.

This spongy lead is remarkably well suited for making models or matrices for galvano-plastic purposes. Under a good press it is converted into a flexible plate of dense metallic lead.—*Jahrb. für Prakt. Pharm.*, xviii. p. 380.

On the Amount of Nitrogen which Birds assimilate from their Food. By J. L. Lassaigne.

We have already had occasion to notice several investigations on the relation of the nitrogen contained in the excrements to that in the food. The results of such researches as were made by Boussingault upon cows and horses have at least shown that the amount of nitrogen of the different kinds of food decreases until their transition into products of digestion. In the course of twenty-four hours cows must absorb 27 grms. and horses 24 grms. nitrogen from the food.

Lassaigne had occasion to make a similar series of experiments on the digestion of birds. For four days the excrements of a goldfinch were carefully collected, and, together with the weight of the food supplied to the bird, carefully noted down. In ninety-six hours it consumed 23·5 grms. millet; during this time the excrements weighed 7·5 grms. The analysis of the millet and of the excrements furnished—

Nitrogen in 1 grm. of millet	0·00708
Nitrogen in 1 grm. of excrements	0·00970

Hence we find that the bird obtained from the whole amount of millet 0·164 grm., and secreted in the excrements 0·072. The difference between these quantities amounts to 0·092, which expresses the amount of nitrogen assimilated by the bird in four days. Dividing by 4, we obtain the daily absorption of 0·023 grm., or about $\frac{1}{2}$ a grain of nitrogen for twenty-four hours.

This quantity of nitrogen, which was assimilated in a day, forms the seventh part of the nitrogen contained in the whole of the millet; the bird must therefore have digested daily 3·81 grms. millet in twenty-four hours. Now since the bird had eaten in four days 23·5 grms., or 5·87 grms. millet in a day, 2·06 grms. must have passed off with the excrements. Consequently in his state of cap-

tivity he digested only three-fifths of the food furnished, which probably would not have been the case if he had been free.

At all events it results from these observations, that in birds, as in mammalia, a certain amount of nitrogen passes from the food into the organism. In twenty-four hours the goldfinch assimilates 0·023 grm., or somewhat less than a grain. The quantity of nitrogen, compared with the amount of food containing it, constitutes $\frac{1}{145}$. On comparing this result with that obtained by Boussingault on horses and cows, a remarkable connexion is found to exist, for the quantities of nitrogen which these animals absorb also in twenty-four hours form $\frac{1}{7}$th of the nitrogen contained in the food for the cow, and for the horse $\frac{1}{6}$th. With respect to the assimilated mass of the food, the nitrogen absorbed amounts to $\frac{1}{119}$th of the food in the case of the cow, and in that of the horse to that of $\frac{1}{68}$th.—*Journ. de Chim. Méd.*, v. p. 621.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 15, 1850. (The President in the Chair.) The following papers were read:—

"On the Preparation of certain Chlorates, particularly of Chlorate of Potash," by F. C. Calvert, Professor of Chemistry to the Royal Institution, Manchester.

The author's method for the preparation of chlorate of potash consists in leading a current of chlorine into a solution of caustic potash mixed with quick-lime. The maximum amount of the chlorate was obtained, when to 1000 fluid grains of a solution of caustic potash, of a specific gravity of 1·100, containing 102·33 grs. of anhydrous potash, 358 grs. of quick-lime were added, and the whole slightly heated. In this experiment, 220 grs. of chlorate of potash were obtained, and at least 20 grs. might be assumed to be left behind in the mother-liquor. When the potash was taken either of greater or less density than the above, the amount of chlorate was diminished. In this process, 100 parts of anhydrous potash give 260 parts of chlorate, in the ordinary process only 43.

"On Propylene, a new Hydrocarbon of the Series C^nH^n," by Captain John Reynolds.

The experiments of the author were made with the view of ascertaining the nature of the gases formed by passing amyle-alcohol through a red-hot tube. At a moderate red heat, in this experiment, gaseous products are obtained, which preliminary experiments proved to be a mixture of gases in variable proportion, which could give no satisfactory results to endiometrical analysis. By treating bottles of the gas with bromine, a heavy liquid was obtained, which, after purification, exhibited a boiling-point of 143°, and a specific

gravity of 1·7. The empirical formula of this body is $C^3 H^3 Br$. From the density of the vapour, however, the author concludes that the formula of this body is $C^6 H^6 Br^2$; the density found by experiment being 7·3098, that calculated 7·0003. He calls this body hydrobromate of bromide of propionyle, $C^6 H^5 Br, HBr$. By the action of an alcoholic solution of potash upon the oil, the substance $C^6 H^5 Br$ is probably formed. The chlorine compound, $C^6 H^6 Cl^2$, was also produced; it is a liquid boiling between 100° and 103°. From these experiments it may be concluded, that the gas which combines with the bromine and chlorine is the hydrocarbon $C^6 H^6$, propylene.

"Note upon the Action of Heat upon Valeric Acid, with some Remarks upon the Formulæ of the Alcohol Radicals," by Dr. A. W. Hofmann.

By the reaction with bromine given by Captain Reynolds, Dr. Hofmann was enabled to detect propylene in the products of the decomposition of valeric acid distilled through a red-hot tube; of this hydrocarbon, the great bulk of that which is produced appears to consist. The experiment was made for the purpose of deciding whether the homologue of marsh gas, the formation of which was expected in this reaction, is identical with the substance called ethyle, as assumed by Laurent and Gerhardt—

$$C^{10} H^{10} O^4 - 2CO^2 = C^3 H^{10} = 2C^4 H^5.$$

If the body thus procured were truly identical with ethyle, it would prove that the formula of the latter should be doubled. In support of this higher formula the author brings forward various arguments,—1st, that the so-called radicals have not the chemical properties which it would be reasonable to attribute to these bodies; 2nd, that the equivalents of these radicals are supposed to be represented by 2 vols. of vapour, which is contrary to all analogy; 3rd, that the boiling-points of the radical hydrocarbons present anomalies irreconcilable with our present knowledge, assuming them to have the formulæ given, but that, doubling their formulæ, these anomalies vanish; 4th, that even the mode of the production of these substances is not precisely analogous to that of the production of hydrogen from hydriodic acid, and that the circumstances of their formation can very well be explained on the other hypothesis. The author concludes by stating, that even if these substances be proved to be no radicals, but members of the marsh-gas series, the greatest interest must attach to them, from the high probability of being able to reproduce from these bodies the members of the series of alcohols.

Society of Arts.

April 24, 1850.

"On the Purification of Coal-Gas," by Mr. Laming.

A paper was read on the above subject, giving some details of Mr. Laming's patent process, whereby he has succeeded in effecting the complete purification of coal-gas, by the chemical action of its own impurities on materials which do not require to be periodically

renewed. The peculiar feature of the invention is, to cause the sulphur in the gas to become spontaneously converted into sulphuric acid, and then to combine with the next greatest impurity, viz. the ammonia, and form sulphate of ammonia, which is a solid and inodorous salt of considerable value. The carbonic acid of the gas, which is mainly instrumental in bringing about these chemical changes, escapes after having done its office, and is got rid of without expense. The author of the paper commenced by observing, that it was surprising that the perfect purification of gas, so important both in a sanitary and commercial point of view, should have excited so little interest in persons capable of investigating the subject; and that now, after nearly half a century, the problem remains as far from a satisfactory solution as ever. That the primitive and palpably imperfect purification by lime should be still universally prevalent may appear blameworthy on the part of the officers to whom public companies have entrusted the internal arrangement of their works; but when the extent and diversity of the duties of a gas engineer and the purely chemical character of gas-making are taken into consideration, it rather excites surprise that the directors have not seen it prudent to aid their engineers by appointing competent and intelligent chemists to assist them. The author then alluded to inventions calculated to aid the lime in its purifying powers, and remarked that none of them pretended to be able to supersede the use of lime altogether. In using lime, the loss of material is so great, that not more than 33 per cent. of the quantity employed is really effective; it removes very little of the ammonia; and its odour, when taken from the purifying vessels, is universally known to be detestable. The process of Mr. Laming has been tried in Paris, and successfully carried out in the Chartered Company's Works at Westminster,—first, on a production of about 7000 cubic feet of gas per hour, and subsequently in purifiers ten feet square. The purifying material virtually consists of a mixture of the two oxides of iron and calcium, which the author sometimes makes by decomposing a saturated solution of muriate of iron by lime or chalk, and then mixing in breeze or sawdust to give to the mass the necessary permeability. This material withdraws from the gas 22 parts of carbonic acid for every 17 parts of ammonia which it removes, besides the sulphuretted hydrogen. The perfection of its action is such, that the gas which has passed through it does not afford the slightest trace, either of ammonia or sulphuretted hydrogen, to the most delicate tests.

While the mixture is being made, the iron becomes peroxidized by the atmosphere, a result which is greatly facilitated by its spontaneously elevated temperature, as well as by the porosity of the mass. The affinities called into play on passing impure coal-gas through this very pervious material, placed instead of lime in the ordinary lime purifiers, are as follows:—The impurities are dissolved in the moisture of the absorbent matter, which is forcibly retained by the hygrometric nature of the muriate of lime also dissolved in it. The sulphuretted hydrogen then combines with the peroxide to

form water and sesquisulphuret of iron. The ammonia, at the same time, is attacked by the carbonic acid, giving up in exchange the sulphuretted hydrogen with which it is in part combined; while, in proportion as the ammonia and carbonic acid unite to form carbonate of ammonia, the latter salt reacts on the muriate of lime, with production of muriate of ammonia and carbonate of lime. When none of the oxide of iron and muriate of lime remains unchanged, the vessel which contains the materials is thrown for a time out of connexion, and the materials are exposed to atmospheric air, by which their purifying powers become regenerated. The affinities in this regeneration are as interesting as those concerned in the gas purification. The oxygen of the air changes the sesquisulphuret of iron into a sulphate of iron; and this salt and the carbonate of lime reciprocally decompose each other, forming sulphate of lime and carbonate of oxide of iron; but as artificial carbonate of iron is not persistent in the presence of atmospheric oxygen, it becomes quickly changed into hydrated peroxide of iron, the carbonic acid escaping into the air.

These changes, brought about by the action of the atmosphere, reproduce the purifying material in its pristine energy, with this difference; that as the process began with muriate of lime combined with the oxide of iron, the process is continued by that oxide mixed with precipitated sulphate of lime, which acts on the carbonate of ammonia in precisely the same way as the muriate of the same base. The regeneration of the used materials is completed in an hour or two, and the author has already effected it as many as fifteen times; there seems, in fact, to be no end to it; but undoubtedly a time must arrive when the accumulated salt of ammonia will need to be washed out; and, when this has been done, the material will be again in all its pristine force.

The advantages of this new process are, that the gas is completely purified, even from its sulphuret of carbon, the most intractable of all its impurities (and that with an increase in illuminating power, which has been estimated as at least 8 per cent.); the materials are inexpensive and susceptible of repeated use an indefinite number of times, with little labour; they give no unpleasant odour when done with; convert the impurities of the gas into marketable products of value; and the wear, tear and cost of apparatus, generally an important item, is reduced to a minimum.

Liebig conceives that peroxide of iron is the purifying agent of the human blood, absorbing oxygen in the lungs, and passing as arterial blood to the various parts of the system, where it combines with organic matter and evolves heat, with the production of carbonate of oxide of iron; in which state it returns as venous blood to the lungs, and is then decomposed, with evolution of carbonic acid and re-formation of peroxide of iron; and so on as before. If this be correct, the resemblance of the two processes is curious and interesting.

THE CHEMICAL GAZETTE.

No. CLXXXIV.—June 15, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Behaviour of some Fatty Oils towards Bichromate of Potash and Sulphuric Acid. *By* G. ARZBÆCHER.

THE decomposition which oleic acid, margaric acid and various oils experience under the influence of nitric acid has been investigated by several chemists. From the beautiful investigations of Laurent, Bromeis and Redtenbacher, we know that oleic acid, under the oxidizing influence of nitric acid, furnishes a series of volatile acids of the general formula $C^{2n} H^{2n} O^4$, whilst the residue consists in part of a series of other acids having the common formula $C^n H^{n-4} O^4$, the first member of which is oxalic acid. Other fats furnish, on the contrary, when treated with nitric acid, principally a single member of each one of these series; thus, for instance, Tilly's investigation has taught that castor oil, under these oxidizing influences, furnishes a volatile product, chiefly œnanthylic acid, and the residue contains suberic and oxalic acids.

The products which are obtained from these substances by other oxidizing agents are as yet unknown; I have therefore made some experiments with chromic acid in the presence of sulphuric acid. I hoped thus to avoid more readily the decomposing influence which the nitric acid exerts upon the products formed, and so to obtain the primary products of decomposition, instead of a series of in part secondary ones. The action of a mixture of bichromate of potash and sulphuric acid upon the oils differs considerably: whilst with castor oil and linseed oil I could only use a very dilute solution of the mixture, I had to employ a comparatively very concentrated solution with stearine, oleine, poppy oil, stearic and margaric acids. The first action on the application of heat is generally very violent; the mass rises, and very acid vapours of a strong smell distil over, and a greater or less number of drops of oil float upon the condensed water. On account of this violent action, at first but little of the above-mentioned solution should be added; as soon as the first frothing is passed, ebullition proceeds quietly. The oil becomes thick; and if the distillation is carried on so that there is sufficient water to prevent the excess of sulphuric acid acting upon the oil and forming sulphurous acid, the oil is converted into a solid black mass when sufficient chromic acid is present.

The oils which I have submitted to more accurate examination are castor oil and poppy oil, because they seemed to me to furnish analogous products.

When castor oil is treated in a retort with a mixture of 4 parts bichromate of potash, 5 parts sulphuric acid and 2 parts water, a violent action results on the application of heat, after which the mixture boils quietly; and if now gradually so much of the hot solution is added as is compatible with the action, a considerable amount of an oil distils over, which floats upon the acid liquid.

The water separated from the oil had a strong peculiar odour and acid reaction; it was saturated with carbonate of baryta, and heated to boiling in a retort. An oily body, which possessed in a high degree the above-mentioned odour, passed over with the aqueous vapour; it was perfectly neutral, and dissolved slightly in water, to which it imparted its odour. As soon as no more of the neutral substance passed over, the distillation was discontinued, the residue filtered and evaporated to dryness in a covered dish on the water-bath. The residue formed a white saline mass, which dissolved in alcohol, and after filtration congealed to a solid mass on cooling. The salt was thrown upon the filter, washed with cold alcohol, and recrystallized from alcohol of 0·848. After this treatment, the salt formed white shining scales, which were scarcely moistened by cold water, but dissolved readily in hot water, and still more readily in alcohol of 0·848, from which it separated almost entirely on cooling. The salt proved on combustion to be œnanthylate of baryta. It furnished—

Carbon	42·14	14	41·98
Hydrogen	7·02	13	6·51
Oxygen	12·57	3	13·07
Baryta	38·27	1	38·44

A silver salt gave 48·64 oxide of silver; the formula $C^{14} H^{13} O^3$, AgO requires 48·66 per cent. silver.

The oil separated from the water contained hydrate of œnanthylic acid and some of the neutral body, as evident from the odour and the reaction. It was saturated with a solution of hydrate of soda, and distilled with water. The residue, decomposed with sulphuric acid, furnished on distillation with water pure colourless hydrate of œnanthylic acid.

The body separated from the œnanthylic acid was removed from the water, distilled alone, then dehydrated with chloride of calcium and rectified; it formed a very mobile colourless liquid, with a pungent taste and peculiar odour, which is but sparingly soluble in water, but soluble in every proportion in alcohol. The alcoholic solution gives, with nitrate of silver and a little ammonia, a white precipitate, which quickly turns black in the light, dissolves with partial decomposition in alcohol, and separates again on cooling. The aqueous solution, heated for some time with nitrate of silver in the water-bath, produces the silver mirror so characteristic of the aldehydes. Nitric acid decomposes it with violence.

By combustion with oxide of copper, numbers were obtained which strengthened the supposition that it belongs to the series of the aldehydes:—

Carbon	69·25
Hydrogen	12·05
Oxygen	18·70

According to these numbers, the carbon is to the hydrogen and oxygen as 5 : 5·3 : 1, or doubled, $C^{10} H^{10} O^2$, which corresponds to the formula of the aldehyde of valerianic acid.

Subsequent experiments must show whether this body is really the aldehyde of valerianic acid, as I had not sufficient material to decide the question with certainty. I tried to oxidize it into valerianic acid by means of hydrate of potash. For this purpose I heated a certain quantity with an alcoholic solution of hydrate of potash on the water-bath until the previous odour had entirely disappeared, and evaporated the brown mass to dryness. It was then decomposed with sulphuric acid, when a brown resinous mass separated, which was removed, and distilled in a flask with water to which a little caustic soda had been added to saturate any acetic acid present. The water which passed over had an acid reaction, and exhibited on the surface some little drops of oil; the whole was saturated with carbonate of baryta, evaporated to dryness in the water-bath, the residue dissolved in alcohol, and set aside to crystallize. From the baryta salt I prepared the silver salt; but the quantity was so small that I could only make a few determinations of the atomic weight, the result of which can of course not be assumed to be decisive. The amount of oxide of silver varied between 53·96 and 54·30 per cent.

Poppy oil, treated in the same manner as the castor oil, furnished the same products, judging from the odour. In the present case a more concentrated solution of the bichromate was used, viz. 4 parts bichromate of potash, 5 sulphuric acid and 6 parts water. When more water is used at the commencement, no action results on the application of heat, and the excess of water distils over with difficulty and with considerable concussions; when the first action is over, a more dilute solution may be used. Care must also be taken, in the present case, that the excess of sulphuric acid does not act upon the undecomposed oil. At 212° but little oil passes over; when the temperature had risen to 248°, I added a dilute boiling solution of the chromate of potash. Between 266°–302° a solid fat passes over. The distillate was saturated with carbonate of baryta, the neutral substance separated by distillation as before, the residue evaporated, and purified by recrystallization from alcohol. The crystalline form of the baryta salt showed at once that I had not to do with the œnanthylate of baryta. The crystals of the first crop were laminar; the last, on the contrary, were in groups, which were soluble in water and alcohol. They were recrystallized once or twice from the latter, and burnt, when they proved to be caproate of baryta, viz.—

Carbon	38·92	12	39·76
Hydrogen	5·91	11	5·95
Oxygen	13·24	3	12·76
Baryta	41·93	1	41·53

As but little baryta salt was obtained in this manner from the acid water, the acids separated from the neutral body were saturated with baryta.

The neutral body from poppy oil perfectly agrees in its external properties with that obtained from castor oil; this was confirmed with respect to its composition by analysis, which gave—

Carbon	68·54
Hydrogen	11·78
Oxygen	19·68

The castor oil appeared to me to furnish far more of the acid product than the poppy oil, and I am inclined to view the method of preparing œnanthylic acid from castor oil by oxidation as not at all unpractical.

Besides these two oils, I also examined oleine as it is obtained from the stearine manufacturers; it however furnished a distillate which had quite a different odour, possessed an acid reaction, and appeared to be similar to those obtained from stearine and rape oil. Linseed oil is the most readily oxidized of all these oils; it likewise gives an acid distillate of a strong odour.—Liebig's *Annalen*, Feb. 1850.

On the Compounds of Sulphocarbaminic Acid. By H. Debus.

The author has made a fresh examination of those bodies which were first obtained by Zeise in the treatment of sulphuret of carbon with ammonia. In this reaction Zeise discovered the sulphocarbonate of ammonia and the hydrosulphuret of the sulphocyanide of ammonium, which latter, according to the author, is something different, viz. the sulphocarbaminate of the sulphuret of ammonium.

When ammonia and sulphuret of carbon act upon each other in the presence of anhydrous alcohol, there are formed,—1st, sulphocarbonate of ammonia and sulphocyanide of ammonium; 2nd, sulphocarbaminate of the sulphuret of ammonium. If the operations are conducted with concentrated liquids, and at a temperature of 86° to 104° F., an excess of ammonia produces chiefly the substances enumerated under 1; while dilute solutions of ammonia in alcohol, excess of sulphuret of carbon, and a temperature of 50° to 60° F. gives rise principally to the formation of the substance mentioned under 2. The preparation of the above compounds has been well described by Zeise.

The Sulphocarbaminate of the Sulphuret of Ammonium, $CNH^2S\,CS^2NH^4S$, crystallizes in long, thin, lemon-coloured prisms, which have a faint odour of sulphuret of ammonium, dissolve easily in water, less readily in alcohol.

Muriatic and sulphuric acids separate the sulphocarbaminic acid

from concentrated aqueous solutions in combination with sulphuretted hydrogen as a colourless oil, which decomposes into different products, among which hydrosulphocyanic acid predominates. Muriatic acid precipitates from dilute solutions of the salt an extremely small quantity of a white flocculent body, which subsequently collects into a liquid, and appears to be sulphuret of carbon. The solution itself smells of cyanic acid, and contains a large amount of sulphocyanic acid.

A solution of the sulphocarbaminate of the sulphuret of ammonium furnishes, with one of the protosulphate of nickel, a yellowish-green precipitate, which dissolves in ammonia and muriatic acid.

When boiled with water, it acquires a dark green colour, while the liquid dissolves sulphocyanic acid. The protosulphate of cobalt behaves in the same manner. Perchloride of mercury gives a white precipitate, which is more copious on the addition of muriatic acid; nitrate of the oxide of uranium produces a blood-red liquid, but no precipitate; sulphate of the protoxide of cerium separates long, shining, colourless needles, which contain no cerium; nitrate of bismuth causes a copious yellow precipitate, which is insoluble in muriatic acid and ammonia, but is turned brown by the latter; arsenious acid gives a white precipitate, which turns yellow and is readily soluble in ammonia; chloride of platinum produces a copious yellowish-brown precipitate, which on boiling with water acquires a dark brown colour, and is insoluble in muriatic acid. On boiling concentrated solutions of sulphocarbaminate of ammonia with sulphate of the oxide of chromium, minute colourless needles separate, which contain chromium and sulphur; after several hours, the mother-liquor deposits a blue substance. Sulphate of cadmium gives a yellowish-white precipitate soluble in muriatic acid; protochloride of tin and perchloride of antimony exhibit a similar behaviour.

The sulphocarbaminate of the sulphuret of ammonium is decomposed in a moist atmosphere into sulphocyanide of ammonium. Heated with solution of caustic potash, it forms sulphuret of potassium, sulphocyanide of potassium, water and ammonia—

$$CNH^2S, CS^2NH^4S + 3KO = 3HO + 2KS + C^2NS, KS + NH^3.$$

Chlorine, iodine and bromine deprive it of ammonium, and produce a substance which has the composition $C^2NH^2S^4$. The sulphocarbaminate of ammonia furnished on analysis—

Carbon	11·31	11·48	2 =	12	10·90
Hydrogen	5·9	5·53	6	6	5·45
Nitrogen	..	..	2	28	
Sulphur	..	..	4	64	

Sulphocarbaminate of the Sulphuret of Lead, C^2NS^3, PbS, is obtained by precipitating the ammonia salt with acetate of lead. It is white, but becomes somewhat red in the drying. Heated with solution of caustic potash, it is decomposed into sulphuret of lead, sulphocyanic acid and sulphuretted hydrogen. On ebullition with

water, the salt turns black, with formation of sulphocyanic acid. Analysis of the salt dried *in vacuo* gave—

Carbon	6·25	2 =	12·0	6·12
Hydrogen	1·13	2	2·0	1·02
Lead	52·30	1	103·8	53·06
Sulphur	..	4	64·0	
Nitrogen	..	1	14·0	

Sulphocarbaminate of the Sulphuret of Zinc, $C^2 H^2 NS^3$, ZnS, is the compound which Zeise regarded as the sulphocarbonate of zinc, and is formed when sulphate of zinc is added to a solution of the ammonia compound until the precipitate is no further dissolved; the whole is then filtered and washed with cold water; it is a white powder. Analysis gave—

Carbon	9·81	2 =	12·0	9·65
Hydrogen	1·88	2	2·0	1·60
Sulphur	..	4	64·0	
Nitrogen	..	1	14·0	
Zinc	..	1	32·3	

Sulphocarbaminate of the Sulphuret of Copper, $C^2 H^2 NS^3$, CuS, is prepared from the ammonia salt with sulphate of copper; it forms a yellow powder, insoluble in water and alcohol. It gave on analysis—

Carbon	9·67	2 =	12·0	9·69
Hydrogen	1·73	2	2·0	1·61
Sulphur	50·90	4	64·0	51·68
Nitrogen	12·11	1	14·0	11·33
Copper	26·32	1	31·8	25·69

If we deduct 2 atoms of water from 2 atoms of the carbonate of ammonia, we have the carbaminate of the oxide of ammonium which was prepared by Laurent. In a manner analogous to this, sulphuret of carbon and ammonia, when both are anhydrous, give sulphocarbaminate of the sulphuret of ammonium. The production of this substance perfectly resembles that of the amminate salts of ammonium produced from the acids $C^n H^n O^4$.

Bicarbonate of ammonia -4 atoms of water gives the formula of cyanic acid, $C^2 O^4 NH^4 O - 4HO = C^2 NO$; and bisulphocarbonate of the sulphuret of ammonium -4 atoms of sulphuretted hydrogen gives sulphocyanic acid, $C^2 S^4, NH^4 S - 4HS = C^2 NS$. The compounds of this substance, which as yet is not known in the isolated state, with those of cyanic acid, may be expressed as follows:—

$$C^2 NS + MS$$
$$C^2 NO + MO,$$

where M denotes a metal or hydrogen.

The compounds $C^2 NS$ and $C^2 NO$ stand, as regards their composition, in the same relation to sulphuret of carbon and carbonic acid as succinimide to succinic acid or as oxalanile to oxalic acid. Sulphocyanic acid and sulphocarbaminic acid are converted by sulphuretted hydrogen, *in statu nascenti*, like cyanic acid and carba-

minic acid by water, into the corresponding non-nitrogenous acids and ammonia.

Cyanic and sulphocyanic acids are moreover sufficiently distinguished from the imides; the two first substances possess decidedly the character of acids, and contain no hydrogen. They are compounds, which certainly contain a different radical from those of which they might be considered to be the imides.

The xanthamide described by the author at page 146 agrees in all its properties with the formula AeO, CNH^2O, CS^2. It is consequently a carbaminate of the oxide of ethyle, in which half its oxygen is replaced by an equivalent amount of sulphur. If we arrange the analogous compounds treated of in this paper together, they will stand in the following relation:—

Carbonate of the oxide of ammonium	$2(NH^4O, CO^2)$.
Carbaminate of the oxide of ammonium	NH^4O, CNH^2O, CO^2.
Cyanate of the oxide of ammonium	NH^4O, C^2NO.
Sulphocarbonate of ammonium	$2(NH^4S, CS^2)$.
Sulphocarbam. of the sulphuret of ammonium	NH^4S, CNH^2S, CS^2.
Sulphocyanide of ammonium	NH^4S, C^2NS.

The formulæ which Debus has proposed for the substances here enumerated agree better with the analyses than those of Zeise. The sulphocarbaminate of the sulphuret of ammonium should have given 12·9 per cent. carbon and 6·5 hydrogen, if it were, according to Zeise, C^2NHS^2, AmS (sulphuretted hydrogen—sulphocyanide of ammonium); the lead salt should have furnished, according to the old formula, 6·7 carbon and 58 per cent. of lead; the zinc sulphuret, 11·2 per cent. carbon; according to the old formula, C^2NHS^3, Zn (sulphocarbonate of zinc, Zeise); and the sulphuret of copper, according to Zeise's formula, 44 per cent. of sulphur; none of which numbers agree so well with the analyses of Debus.

All the bodies above described are decomposed at a gentle heat, and under the influence of alkalies, into sulphuretted hydrogen, sulphocyanic acid and a sulphuret. They must therefore be treated at as low a temperature as possible.—Liebig's *Annalen*, lxxiii. p. 26.

On the Nitrates of the Protoxide of Mercury. By Prof. Marignac.

The various statements of those chemists who have examined the combinations of the protoxide of mercury with nitric acid, especially Lefort and Mitscherlich, differ considerably from each other; and much uncertainty exists in the descriptions of these salts, from so little attention having been paid to the form of the crystals.

Marignac never obtained more than three different salts in the action of nitric acid upon mercury. They are procured by allowing nitric acid, which has been diluted with twice or thrice its bulk of water, to act upon excess of metallic mercury. The action, which is violent at first, gradually slackens; and if the still hot and strongly acid solution is then decanted, tolerably large prismatic crystals separate on cooling. The most perfect are removed, and the re-

mainder heated with the mother-liquor and excess of mercury. After a time the liquid is again poured off, and deposits on cooling a fresh crop of crystals. This operation is repeated as long as the crystals which form remain the same. In the analyses of these compounds, the water and nitric acid must not be determined from the loss. The nitric acid is calculated from the quantities of nitrogen which these salts disengage when calcined with metallic copper only.

Neutral Nitrate of the Protoxide of Mercury, $Hg^2, NO^5 + 2HO$, is the salt described by Lefort as the *nitrate biatomique acide*. It has an acid reaction, and is formed in the first crystallization. The form of the crystals may be derived from an oblique rhombic prism; but in general the planes of the prisms are very much shortened, and the crystals have the appearance of an octahedron with rectangular base, and some resemblance to a rhombohedron. In some rare cases very long prisms occur.

These crystals are colourless, fragile, and frequently of laminar structure. They gradually effloresce in dry air, and contain much mother-liquor enclosed. The following analysis leads to the same formula as Mitscherlich proposed for this salt. It differs, on the other hand, from that of Lefort, who admits in the crystallized salt $2(Hg^2 O, NO^5) + \frac{1}{2} HO$, and in the salt dried over sulphuric acid $2(Hg^2 O, NO^5) + HO$. Lefort has described the crystals as obtuse rhombohedra, which is likewise opposed to the results of the author's investigations. The crystalline salt contained 6·97, 6·69 and 6·53 per cent., or 2 atoms of water; that dried over sulphuric acid gave—

Protoxide of mercury	78·95	79·18	1 = 2600		79·39
Nitrogen	5·56	..	1	175	5·34
Oxygen	..	..	5	500	15·27
Water	0·54				

$\frac{4}{5}$-*Basic Nitrate of the Protoxide of Mercury*, $3(Hg^2 O, NO^5) + (Hg^2 O, HO)$, is the salt described by Lefort as *nitrate intermediare*, with the formula $3Hg^2 O, 2NO^5 + \frac{5}{2} HO$. This formula is not correctly determined. The salt is obtained in flattened needles, sometimes in pretty good, but always very long and thin prisms. The crystals are perfectly colourless, shining and transparent, and do not effloresce in the air on drying over sulphuric acid. They may be kept for some time in the water-bath at 212° without altering in appearance or in weight; but in the course of time they become yellow and decrease in weight. Their form is a right rhombic prism of 83° 52′, which appears considerably flattened by the truncation of the obtuse edges. The crystals always exhibit the basic terminal surface, frequently without any modification, but sometimes also other less developed surfaces. The salt for analysis was dried over sulphuric acid; it scarcely lost a trace of moisture, and was therefore analysed in the hydrated state. It furnished—

Protoxide of mercury ..	82·48	..	..	4 = 10400·0		82·95
Nitrogen	4·49	4·27	4·21	3	525·0	4·19
Oxygen	..	..	..	15	1500·0	11·96
Water	1·33	1·26	1·07	1	112·5	0·90

$\frac{2}{3}$-*Basic Nitrate of the Protoxide of Mercury*, $3(Hg^2O, NO^5)+2(H^2O, HO)$, is the salt described by Lefort as the *nitrate biatomique neutre* with the incorrect formula $2Hg^2O, NO^5+2HO$. It contains 1 atom hydrated protoxide of mercury more than the preceding salt.

It is readily and constantly obtained when the mother-liquors from the preceding $\frac{1}{3}$-basic salt are boiled for some hours with an excess of mercury, and the evaporating water renewed. On cooling, prismatic crystals separate, frequently of considerable size. It is also formed gradually when the crystals of the preceding salt are left in contact, at the ordinary temperature, with their mother-liquor and metallic mercury. This salt is perfectly colourless; it is not altered *in vacuo*, nor in the water-bath at 212°, unless left in for too long a time. Its crystalline form belongs to the system of the doubly oblique rhombic prism, and its modifications are very numerous, the development of the different systems of surfaces varying very much. The salt was dried *in vacuo* for analysis; it gave—

Protoxide of mercury....	85·15	..	..	5	=13000	85·24
Nitrogen.....	3·48	3·46	3·42	3	525	3·44
Oxygen	..	..	..	15	1500	9·84
Water.....	1·74	1·71	..	2	225	1·48

Bibasic Nitrate of the Protoxide of Mercury, $2Hg^2O, NO^5+HO$ or Hg^2O, NO^5+Hg^2O, HO.—When the neutral salt is dissolved by a gentle heat in water, and then so little water added that the liquid does not become turbid, a colourless crystalline precipitate gradually forms, which appears to be the $\frac{2}{3}$-basic nitrate. If a larger quantity of water is added at once, the solution becomes turbid, and deposits a light sulphur-yellow precipitate, which appears not to be at all altered by cold water. Only by very long-continued washing is its colour changed into gray, which indicates further decomposition and the elimination of mercury. The first action of the water removes a portion of the acid from the protonitrate of mercury, and converts it into a bibasic salt, upon which cold water exerts but a very slow decomposing action. When the yellow salt is boiled with water, it immediately turns black. This salt was repeatedly washed, and then dried at a temperature of 104°–122°. It retained its pure yellow colour, and gave on analysis—

Protoxide of mercury	86·76	2 =	5200·0	86·85
Nitrogen	3·03	1	175·0	2·92
Oxygen.....	..	5	500·0	8·35
Water	2·06	1	112·5	1·88

This analysis confirms that made by Kane of the same salt. Mitscherlich and Lefort prepared this salt, but did not analyse it.—*Ann. de Chim. et de Phys.*, xxvii. p. 315.

On the Composition of the Precipitate which the Subacetate of Lead produces in the Soluble Cyanides. *By* E. Erlenmeyer.

When prussic acid is added to subacetate of lead, no precipitate is formed; it is only on the addition of a certain quantity of am-

monia that a white powder subsides. For analysis, the author washed it with water deprived of carbonic acid, collected it upon a filter, and dried it in watch-glasses under a bell-glass inclosing burnt lime and sulphuric acid. In the drying, the precipitate, the colour of which gradually passes from white to yellow, continually disengages prussic acid, but when once dry the decomposition stops. This precipitate contains, in the dry state, according to the author, 2PbO, PbCy.

Its composition is the same whether aqueous or alcoholic solutions, ammonia or potash are employed. The author adds, that it appears probable that the white precipitate is at first cyanide of lead, which is slowly decomposed by the water into prussic acid and oxide of lead. The decomposition is arrested when the substance has the composition indicated by the preceding formula.—*Journ. für Prakt. Chem.*, xlviii. p. 356.

On the Iodide of Cyanogen. *By* Dr. C. Herzog.

The author has made some further experiments with the iodide of cyanogen obtained by Klobach in refining some iodine*. The material which served for the investigation consisted of the crystals of the iodide of cyanogen which had been freed from adherent iodine by treatment with mercury.

This iodide of cyanogen forms colourless, delicate, flexible needles, with a silky vitreous lustre, resembling caffeine. It has an extremely pungent taste; if the point of the tongue be touched with one of the slender crystals, it causes a sensation like oil of mustard. It is volatile at 50° F., sparingly soluble in cold, but readily soluble in hot water, alcohol and æther. If dissolved in æther or absolute alcohol, a portion of the iodide of cyanogen crystallizes on evaporation in long beautiful needles, which resemble the fibres of the shaft of a pen. In most acids, even in sulphuric, muriatic and nitric acids, it dissolves at the ordinary temperature without decomposition. Chlorine-water does not decompose it, but the iodide of cyanogen dissolves in it to a perfectly colourless liquid. The aqueous solution of the iodide of cyanogen has no action upon solutions of copper, iron, zinc, lead, silver, gold and platinum; but on being shaken with the metals, iodine is eliminated, with the formation of iodides and small quantities of cyanides.

At an elevated temperature, it is decomposed by sulphuric and muriatic acids; nitric acid produces, even on ebullition, no perceptible change, and the liquid remains colourless. In solution of ammonia it dissolves at first unaltered; the solution in an alcoholic solution of ammonia soon deposits crystals of iodide of cyanogen and ammonia.

It had already been noticed by F. Meyer, who first drew attention to the occurrence of iodide of cyanogen in iodine, that iodide of potassium which had been prepared with such iodine, might, under

* Chem. Gaz., p. 159 of the present volume.

certain circumstances, contain cyanide of potassium. In respect to this, the author states, that, after treating iodine with which some iodide of cyanogen had been mixed with metallic iron and water, some protocyanide of iron was found with the protiodide of iron in the solution formed, the former of which must have dissolved in the latter. If the iron be then separated by carbonate of potash, even when previously some iodine containing cyanide has been added, no more cyanogen can be detected in the liquid; the cyanide of iron is consequently contained in the precipitate. When therefore the iodide of potassium is prepared according to the Hanoverian or older Prussian pharmacopœia, with potash and the iodine employed contains iodide of cyanogen, cyanide of potassium is contained in the salt; but when the iodide of potassium is prepared from iodide of iron according to the Hessian or new Prussian pharmacopœia, it contains no cyanide of potassium. On analysis, the author obtained 81·87–82·90 per cent. of iodine.—*Archiv der Pharm.*, lxi. p. 129.

Test for the Presence of Chloroform. By Dr. Snow.

The author placed on the table, at the last meeting of the Westminster Medical Society, the apparatus which he used for detecting the presence of chloroform in a dead body of the housekeeper in the late mysterious affair at Clapham. He said that the process was a modification of one described in the 'Journal du Chimie Médicale' for March 1849. The blood, or portion of the body to be examined, was put into a flask, from which there proceeded a tube, which was made red-hot in part of its course. Another glass tube, attached to the extremity of the latter, was moistened inside with a solution of nitrate of silver, and terminated in a Woulfe's bottle, the interior of which was also moistened with the same solution. Heat being applied to the flask by means of the chloride of calcium bath, the vapour given off had to pass through the red-hot tube, and any chloroform which might be present was decomposed; and the chlorine and hydrochloric acid gas, being set free, were arrested in the next tube, where they formed a white precipitate of chloride of silver, which became rapidly darkened in colour by the action of light. The nature of the precipitate could be further proved by cutting the tube with a file, and introducing a drop or two of nitric acid into one portion and of solution of ammonia into the other. He had distinctly detected the presence of chloroform by this process in two kittens, killed by inhaling the vapour, on six successive days after the death of the animals, although no precautions were taken to protect the bodies from the air, and the quantity inhaled by each kitten must have been less than one minim. The parts of the animals examined were the viscera of the chest and abdomen, the brains and the muscles of the body and extremities. From all these parts clear evidences of the presence of chloroform were obtained. He had also obtained a precipitate of chloride of silver by operating on some portions of the muscles taken from the leg of a child amputated under the influence of chloroform at St. George's

Hospital. The process indeed was one of such delicacy, that he had been able to clearly detect the presence of the hundredth part of a grain of chloroform when dissolved in a thousand grains of water. The only substances which could yield chloride of silver by this method were Dutch liquid, chloride of ethyle, and some other bodies similar in composition and effects to chloroform, but which, however, were not in common use, or even kept on sale. There were chlorides in the human body, but these could not be decomposed below a red heat, and certainly not till the part became dry; whilst in the process he employed, the heat to which the part under examination was exposed was only that of boiling water, or a very little more, and it could not become dry in the most protracted examination, as the greater part of the moisture given off became condensed in the tube, which inclined upwards, and flowed back into the flask. The method, therefore, was liable to no fallacy or objection. He had received from Mr. John Parrott some portions of the viscera of a woman, lately found dead, under very mysterious circumstances, in the Wandsworth-road. The parts had been closed up air-tight from the time they were taken from the body. They included a portion of the brain and of the liver; and though they were kept boiling for two or three hours in their own serosity, not the least trace of chloride of silver was obtained; whilst in the instances where chloroform had caused death, the precipitate began to appear when the heat to which the part was exposed reached to about the boiling-point. In the muscle taken from the child's leg, the chloroform was only a few minutes longer in being detected, although the quantity present must necessarily have been much less than in a case where death had been caused by it.—*Lancet.*

On Cathartine. *By* F. L. Winckler.

The author has prepared and examined the bitter principle from the ripe berries of *Rhamnus cathartica.* The berries were collected towards the end of October, crushed, and the pulp kept for forty-eight hours in a cool spot, then pressed, and the juice, which has a disagreeable sweetish-bitter taste, evaporated to a syrup. Of this residue, 4 oz. were well-agitated with 96 oz. of cold alcohol of 0·833 spec. grav., the extract poured off, and the residue exhausted by further treatment with alcohol. The residue consisted of a viscous, dark blue, turpentine-like mass, of slightly bitter taste, and which, like the juice not exhausted with alcohol, acquired, on addition of a solution of alum and of basic carbonate of potash, a beautiful green colour.

The mixed spirituous extracts, after filtration, had a reddish-brown colour. They were considerably decolorized by animal charcoal, and left, on evaporation in the water-bath, 14 drms. of a dark greenish-brown residue, of thick syrupy consistence, which had a strongly bitter taste, and which, in the course of some days, changed into a tolerably solid, opake, distinctly crystalline mass, of a dark greenish-brown colour. This mass was exhausted with alcohol of

0·863, when about half remained as a dirty olive-green powder, which, after being washed with alcohol, had no longer a bitter, but a sweet taste, and dried in the air to a loose powder.

The spirituous extract was of an intense brownish-yellow colour, had a nauseous and extremely bitter taste, and could be so far decolorized by treatment with animal charcoal that it acquired a pale sherry colour. On evaporation of the alcohol, 7·5 drms. of a dark reddish-brown, almost transparent syrup were obtained, which dissolved in every proportion in water and alcohol, possessed a disagreeable bitter taste, and was almost entirely precipitated by æther from the solution in alcohol. In this state this residue has all the properties ascribed to cathartine; but it is easy to be convinced, from the colour and the avidity with which it attracts moisture, that the substance is not pure.

The bitter principle was obtained in a pure state, according to Winckler, by treating the previously-described mass with about three times its weight of alcohol of 0·833, and mixing the solution with from 8 to 10 times its bulk of æther, in such manner that the liquids do not mix at the commencement; it is then agitated all at once until a viscous mass of grape-sugar, cathartine and extract has separated on the sides of the vessel. The very turbid liquid is now poured into another glass, and the mixture left until it has become perfectly clear. It is then poured off from the viscous sediment, decolorized by animal charcoal and evaporated at a gentle heat, the residue dried in a water-bath and rubbed to powder. The author calls this substance cathartine. It consists of a pale golden-yellow powder, which burns without residue, and dissolves in every proportion in water and alcohol, but not in æther. Its aqueous solution is clear, nearly colourless, and has a disagreeable bitter taste, like a solution of bitter aloes freed from resin. It is neutral towards litmus and curcuma, and furnishes very peculiar reactions with perchloride of iron and basic acetate of lead. The perchloride of iron does not cause a precipitate in the solution of the bitter substance, but strikes a dark brownish-green colour; basic acetate of lead and the alkalies colour the solution golden-yellow, without forming precipitates. The reaction with basic acetate of lead shows the absence of tannin, although the test with iron appears to indicate its presence. Cathartine fuses, when heated over a spirit-lamp, to a yellowish oily liquid, then takes fire, with disengagement of brown vapours of a peculiar odour, and leaves a very bulky cinder, which burns with difficulty.

The bitter substance separated in the preparation of cathartine with alcohol of 0·863, dissolves with a dark greenish colour in water. With alcohol of 0·833, a dark grass-green solution of it was obtained, which could be very nearly decolorized by animal charcoal. The filtered liquid furnished, on slow evaporation, a yellow, verrucoid, crystalline mass, which dissolved in every proportion in water, in considerable quantity in alcohol of 0·833, but was entirely insoluble in æther. On repeated solution in alcohol and recrystallization, the crystalline substance was recognised to be grape-sugar.

On comparing these results with the description of rhamnine by Henry, the author considers it as not improbable that the rhamnine, in the perfect ripening of the berries, is resolved into cathartine and grape-sugar, and that it can consequently only be obtained from the unripe berries. This circumstance deserves attention in relation to its bearing upon medicinal preparations, as it shows that further information is needed to know when to employ ripe and when unripe berries, &c.—*Jahrb. für Prakt. Pharm.*, xix. p. 223.

Observations on the Nitruret of Boron. *By* Prof. Wöhler.

About eight years ago Mr. Balmain discovered a compound of boron with nitrogen, to which, owing to its supposed property of entering into combination with metals like cyanogen, he gave the analogous name of æthogen*. He subsequently found that all the substances described by him as æthonides were the same substance, the nitruret of boron, without any essential amount of metal. He obtained this compound by heating boracic acid with cyanide of potassium, with cyanide of zinc, or with percyanide of mercury and sulphur. I subsequently found that it might also be advantageously prepared by heating to redness a mixture of dry borax and ferrocyanide of potassium.

The observation, that, on heating tungstate of potash with chloride of ammonium, nitruret of tungsten is formed†, induced me to try to prepare the nitruret of boron in the same way. The result entirely corresponded to my expectation. I obtained a body which possesses all the properties of the compound prepared by Balmain with the aid of the cyanides, and which, as I shall show further on, consists of BN; and is consequently so constituted that it is converted by water exactly into boracic acid and ammonia.

To prepare the nitruret of boron in this manner, 1 part of pure and perfectly anhydrous borax is mixed very intimately with 2 parts of dry chloride of ammonium, the mixture filled into a porcelain, or better still, platinum crucible, and heated with the lid on to redness. An ordinary clay crucible is less adapted, because the product may contain a large quantity of iron, owing to the formation of perchloride of iron. Small quantities can even be prepared in glass vessels. A white, porous, but not fused mass, is obtained, which is reduced to a fine powder, and boiled for a long time with a large quantity of water to which some muriatic acid has been added‡. The nitruret of boron then separates as a white powder, which is collected upon a filter, washed completely with hot water, and dried. If it has been prepared in a clay crucible, or with impure unrefined borax, it is necessary to digest it with concentrated hydrochloric acid to remove the impurities, which is not effected with certainty even by this treatment.

* Phil. Mag., vol xxii. p. 467. † Chem. Gaz., p. 161 of the present volume

‡ When pure water is first used, and the filtered solution is evaporated slowly, chloride of sodium separates in very distinct transparent octahedra. When heated, they turn milk-white, without losing their form or their lustre. From their solution in water they are reobtained in cubes.

Prepared in this manner, the nitruret of boron forms a perfectly white light powder, which, even with a magnifying power of 500, appears as an entirely amorphous, granular, milk-white mass. When rubbed into the skin it renders it very smooth. It possesses all the characteristic properties ascribed to it by Balmain; held in the margin of a flame, it evolves a brilliant greenish-white light; it disengages abundance of ammonia when fused with hydrate of potash; and is not changed either by concentrated acids or concentrated alkalies, nor by ignition in hydrogen or chlorine gas. In a current of aqueous vapour, even at a moderate red heat, it is entirely converted into ammonia and boracic acid, when the latter is for the greater part volatilized with the aqueous vapours, so that on condensation a solution of borate of ammonia is obtained.

The nitruret of boron was not in the least altered by being exposed for one hour to the fusing-point of nickel in a porcelain crucible placed in a clay crucible, and surrounded by charcoal powder; it neither fused nor lost nitrogen.

In a spirit-flame fed with oxygen it burns quickly, with a slight greenish-white flame, and with formation of boracic acid vapour. On the other hand, it cannot be made to burn when heated in a small porcelain crucible to perfect redness by passing oxygen upon it. It does not even give off light; and indeed its remarkable property of being more brilliantly phosphorescent than any other body, with a greenish-white light, only occurs in contact with the flame, and is always connected with oxidation, even though this is exceedingly slow. That which had been heated to redness in chlorine gas appeared to me to evolve a remarkably brilliant light, whilst, on the contrary, impurities seem to prevent the luminosity altogether.

Another extremely characteristic property of the nitruret of boron is that of forming deutoxide of nitrogen or nitrous acid, when heated to redness with easily reducible metallic oxides. When heated in a glass tube with oxide of lead, oxide of copper or peroxide of mercury, the tube becomes quite filled with red fumes.

Heated with water in a sealed glass tube to 392°, it forms ammonia and boracic acid; however, the change proceeds but very slowly at this temperature. If the action is continued for several hours, the glass is found, if the tube has not exploded, deeply eaten into, and converted into a white substance resembling opal. The water is found to contain potash, silicic acid, boracic acid and free ammonia.

Although hot concentrated sulphuric acid has no effect upon the nitruret of boron when allowed to act upon it but for a short time, it is nevertheless converted by it, although but very slowly, into ammonia and boracic acid, when heated for a long time, until part of the acid is volatilized. It is more readily decomposed by digestion with fuming hydrofluoric acid, with the formation of much fluoboride of ammonium.

The most remarkable reaction is exhibited by the nitruret of boron on ignition with anhydrous carbonate of potash; it is resolved precisely into borate and cyanate of potash; it consequently decom-

poses the carbonic acid, reducing it to carbon, which combines with the nitrogen to form cyanogen, certainly a most unexpected mode of formation of cyanogen, which however is in perfect accordance with the observation made by Berzelius, that free boron, heated with carbonate of potash, is oxidized at the expense of the carbonic acid, from which it separates the carbon. 1 atom nitruret of boron and 2 atoms carbonate of potash ($BN+2KO, CO^2$) contain the same elements to the same amount as 1 atom borate and 1 atom cyanate of potash (KO, BO^3+KO, C^2NO). This reciprocal decomposition takes place very readily at a faint red heat, in a platinum crucible, over a large spirit-lamp. When a mixture of nitruret of boron and dry carbonate of potash in the above atomic proportions (3 : 17) is heated, it fuses at a temperature at which carbonate of potash alone would not fuse, forming a liquid which on cooling solidifies to a very crystalline white mass. It now consists of nearly equal parts by weight of borate and cyanate of potash, and dissolves in water, yielding a clear solution; I have prepared from it beautifully crystallized pure urea, and from this latter crystallized cyanuric acid. If an excess of nitruret of boron is used, much cyanide of potassium is simultaneously formed, from which I was able to prepare prussian blue and prussic acid. Nitruret of boron, exposed to a strong red heat with free carbonic acid gas in a porcelain tube, does not decompose it.

With respect to the direct proofs of the composition of nitruret of boron, the analyses made with substance of different preparations led at first to very discordant results, and merely proved that this substance, when not prepared with every care, is obtained of dissimilar composition, *i. e.* retaining most tenaciously some foreign admixtures, apparently chiefly boracic acid. I shall not enumerate these experiments, as they have no further value, and will only give those which were made with more carefully prepared substance, and furnished results closely agreeing with each other.

Considering the facility with which the nitruret of boron forms ammonia with the hydrates, there could be no difficulty in determining the amount of nitrogen. It was effected, as in the case of an organic substance, by ignition with soda-lime, which contained somewhat more hydrate of soda than usual to render it more fusible. Four analyses with substances of different preparations, made by Dr. Städeler, furnished 48·13, 49·63, 50·77 and 51·36 per cent. of nitrogen. The nitruret of boron used for the last analyses, which gave 51·36 per cent. of nitrogen, had been treated with hydrofluoric acid. 0·289 grm. gave 2·363 ammonio-chloride of platinum.

Only one plan remained for the direct determination of the amount of boron—oxidation by ignition with an accurately weighed quantity of nitrate of lead. What the fused residue weighed more than the oxide of lead which should remain could only be boracic acid. This method, which may probably find application in many other cases, is easily and quickly performed, and appears to me to furnish satisfactory results. For this purpose, the salt must be perfectly pure and rubbed to a very fine powder. As it is readily de-

composed at a moderate heat, it must be dried with care. The fusion may be effected in a platinum crucible if a large excess of salt be used; but if too little is taken, lead is reduced, and forms an alloy with the platinum. The mixing of the substance to be oxidized with the salt is made in the crucible with a thick polished platinum wire; it must be done very carefully. As the mass puffs up pretty considerably, a gentle heat is applied at first; it is afterwards heated to redness for a few minutes until the mass is perfectly liquid.

0·180 grm. of the nitruret of boron, after being treated with hydrofluoric acid, dried at 302°, and fused with 6·068 grms. nitrate of lead, gave 4·334 fused residue; deducting the amount of lead contained in the salt, =4·088, there remains 0·246 for the generated boracic acid, containing 0·0768 boron, or 42·66 in the nitruret of boron. A second experiment gave 42·23. Five other experiments, made with nitruret of boron of three different preparations, furnished 41·93, 41·61, 40·88, 40·87, 40·38 per cent. of boron.

Assuming the highest numbers found for the nitrogen and boron to be the most correct, we obtain in 100 parts—

Boron	42·66
Nitrogen	51·36
Loss	5·98

This loss can only be oxygen, and is undoubtedly contained in the compound in the form of boracic acid, since special experiments have shown that it contains neither chlorine nor sodium. Calculated in equivalents, the above composition would correspond to a combination of 1 equiv. boracic acid with 14 equivs. of nitruret of boron (BO^3+14BN), which would contain—

Boron	42·617
Nitrogen	51·124
Oxygen	6·259

A compound in such proportions is extremely improbable. It is far more likely that the varying amount of boracic acid (owing to the mode of formation and of the perfectly unfused amorphous state of the nitruret of boron) is only mechanically contained in this, and cannot be removed by the usual solvents; just as sugar, for instance, mixed with boracic acid and carbonized, would furnish a cinder from which probably the whole amount of boracic acid could not be extracted by treatment with solvents.

Pure nitruret of boron (BN), which consequently has hitherto never been prepared, unless that obtained by Balmain's process, which has never been analysed, should prove to be such, would contain in 100 parts,—boron, 43·76, and nitrogen, 46·24.—*Göttingen Nachrichten*, 1850, No. vii.

On the Alcohate and Nitrates of Magnesia. *By* A. Chodnew.

In the year 1827 Professor Graham drew the attention of chemists to a remarkable group of compounds, which, on account of

their analogy with the hydrates, he called *alcohates*. According to his opinion, absolute alcohol possessed the capacity of forming, with some anhydrous salts, combinations in which the alcohol supplied the place of the water of crystallization; and although the idea of replacement of water by alcohol, equivalent for equivalent, is not combined with the term *alcohate*, still it may be considered as the most suitable for these compounds, in the examination of which I came to the following conclusions:—

1. The hexhydrated nitrate of magnesia does not crystallize, as Einbrodt says, in very long parallelopipeds with a strictly square base; but forms, as has been known for some time, rhombic prisms, among which, as I have convinced myself, other derived crystalline forms of the prismatic system are met with.

2. The hexhydrated nitrate of magnesia is, contrary to Einbrodt's statements, a very deliquescent salt.

3. The monohydrated nitrate of magnesia is easily formed, as has already been proved by Graham, and the contrary opinion of Einbrodt is thus refuted.

4. The formation of anhydrous nitrate of magnesia is likewise not difficult, although it cannot be obtained without adding some basic salt. This circumstance is however not prejudicial to the formation of the alcohate of the nitrate of magnesia. The existence of the anhydrous salt was consequently rejected by Einbrodt without any reason.

5. Over sulphuric acid the hexhydrated nitrate of magnesia loses 4 atoms of water, and the bihydrated salt ultimately remains.

6. If the anhydrous nitrate of magnesia be decomposed by heat, a triple basic salt is first formed, which is ultimately decomposed into nitric acid (nitrous acid and oxygen) and magnesia.

7. The old opinion of Fourcroy concerning the existence of the double salt of nitrate of magnesia and nitrate of ammonia must be given up.

8. Anhydrous nitrate of magnesia forms with alcohol a combination, an alcohate, which consists of 3 atoms of alcohol and 1 atom of anhydrous nitrate of magnesia. It is very likely that there exists also a compound of nitrate of magnesia, alcohol and water.

9. Anhydrous chloride of calcium, dissolved in nearly perfectly anhydrous alcohol, forms an alcohate which is composed of 2 atoms of alcohol and 1 atom of chloride of calcium. With great probability it may also be presumed that there exists another alcohate of the chloride of calcium, consisting of 3 atoms of the chloride of calcium, 2 atoms of alcohol and 2 atoms of water; consequently,

10. The compounds discovered by Graham, and denominated by him *alcohates*, are not mechanical mixtures, but real chemical compounds. It is indeed true that he has given no explicit analysis of them, and thus afforded room for doubting the correctness of their composition; but it was no reason why the existence of these interesting compounds should have been denied, without a single experiment being made to examine the truth of Professor Graham's statements.—*Ann. der Chem. und Pharm.*, lxxi.

Remarks on Mr. Kemp's *Apparatus for regulating the Heat produced by a Gas-burner.*

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—Referring to Mr. Kemp's ingenious and useful contrivance for regulating temperature, described in your No. 182, I beg to offer the following suggestion.

Instead of making any "small hole" in the inner tube C, opposite F, let the extremity of the tube C be cut, or ground off, on one side, so as to form a long narrow slit, and leave everything else as it is.

The effect will be, that the mercury, instead of, as at present, opening and closing the aperture of C suddenly and by fits and starts, will do so gradually and proportionately to the temperature.

If the extremity of the tube C be formed into a cone, like an inverted funnel, and then a portion of the side cut off, the area of the aperture for the passage of the gas will form a parabola, or hyperbola, as required, by which the flow of gas may be regulated with great nicety to the temperature needed, and also in any desired ratio.

A platinum wire, or strip of platinum foil, may be welded by the blowpipe to the lips of the aperture, to ensure metallic contact with the mercury; or the interior of the tube might be, for a short space, electrotyped with platinum.

I am, Sir, yours respectfully,
W. K. Westly.

Leeds, May 21, 1850.

On the Constituents and Use of the Jerusalem Artichoke. *By* Messrs. Payen, Poinsot *and* Férey.

The Jerusalem artichokes which the authors used for their experiments were grown upon a sandy soil of moderate goodness, which had been manured with ammonio-phosphate of magnesia. They contained, in 100 parts, 76·04 water and 23·96 dry substance. The dry substance yielded on combustion 4·24 ash and 2·16 nitrogen. This is twice as much as is obtained from potatoes, and somewhat more than the cerealia contain.

There was further obtained from 100 parts of Jerusalem artichoke 0·87 of fatty matters, of which one was liquid, the other solid. This quantity is likewise twice as great as in the potato. Water to which a little muriatic acid was added extracted 1·56 per cent. pecten, which was precipitated by spirit. The insoluble residue was treated with water to which one-twentieth ammonia was added, and expressed. It furnished an aqueous liquid, from which muriatic acid precipitated gelatinous pectic acid, which after washing and pressure amounted to 3·76 per cent.

The dry substance, wholly exhausted with æther, was now washed

with alcohol of 0·850 and 0·833. The crude saccharine matter was thus obtained, but still mixed with a little chloride of potassium and nitrogenous substance. It formed 68 per cent. of the dry substance, or 16 per cent. glucose for the fresh tubers. This large amount of sugar induced the authors to repeat the experiment. The tubers were rubbed to a paste and fermented; from the alcohol obtained 14·7 per cent. of glucose was calculated. Besides these constituents, albumen, gum, and two other nitrogenous matters, were detected in the tubers. The following are the tabulated results of the analysis:—

Water	76·04
Glucose and other saccharine substances	14·70
Albumen and two other nitrogenous substances	3·12
Cellulose	1·50
Inuline	1·86
Pectic acid	0·92
Pectine	0·20
Salts	1·29
	100·00

The ash of the Jerusalem artichoke contained the following constituents. I. is the analyses of some that were grown upon a soil manured with ammonio-phosphate of magnesia, and II. of purchased tubers:—

	I.	II.
Silica	2·00	6·95
Carbonate of lime	4·12	10·23
Carbonate of magnesia	1·94	
Phosphate of lime and magnesia	33·59	16·62
Alumina	1·44	
Chloride of potassium	8·36	10·75
Sulphate of potash	11·16	10·66
Phosphate of potash	28·40	8·45
Carbonate of potash and traces of soda	9·93	36·34

The Jerusalem artichoke also contains a small quantity of a violet pigment, which is deposited in the cellular tissue beneath the epidermis.

According to this investigation, therefore, 100 parts of the Jerusalem artichoke contain 23·96 parts of nutritive substance, and they are certainly well-adapted for the fattening of pigs and cattle.—*Journ. de Pharm.*, xvi. p. 434.

THE CHEMICAL GAZETTE.

No. CLXXXV.—July 1, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Chlorine upon Metallic Chlorides in presence of the Alkaline Chlorides. By MM. SOBRERO *and* SELMI.

THE metallic chlorides upon which we have chiefly experimented are the protochloride of manganese, MnCl, and the protochloride of lead, PbCl. A few experiments have been made with some other chlorides; but the results obtained not being sufficiently precise, we shall reserve their publication for some future occasion.

Chlorine and Protochloride of Manganese with the Alkaline Chlorides.—It is well known that the protochloride of manganese dissolved in water is not altered when submitted to the action of chlorine gas. This is no longer the case whenever the solution of the protochloride of manganese contains a chloride of an alkali (potassium, sodium, calcium, &c.). In this case the chlorine exercises a very lively reaction, for no sooner is it brought into the presence of the salt than it decomposes it, producing a precipitate of the peroxide of manganese. The experiment may be made by passing a current of chlorine into a solution of very pure chloride of sodium or potassium, to which a few drops of protochloride of manganese have been added, or by adding a solution of the metallic chloride to the solution of the alkaline chloride previously saturated with chlorine. This reaction is effected without the assistance of solar light; in fact our experiments were always made with liquids saturated with chlorine in the dark.

M. Millon has described a method by means of which it may be ascertained whether water saturated with chlorine has experienced the direct action of sunlight; in chlorine-water modified by this agent there exists simultaneously hydrochloric and hypochlorous acids; and if some protochloride of manganese be added, it is instantly decomposed with precipitation of the deutoxide. This test is very sensitive, and will detect a very minute trace of hypochlorous acid.

We have repeated the experiments of M. Millon, and we are convinced that his test is very effective in those cases in which the water contains no alkaline chlorides; but that if it contains even the smallest quantity of those salts, it is rendered turbid by the protochloride of manganese, although it has not experienced the action

of the solar rays. Before employing M. Millon's test therefore it will be requisite to ascertain that the chlorine-water is free from alkaline chlorides.

Chlorine and Protochloride of Lead with the Alkaline Chlorides.—M. Millon has observed that the protochloride of lead is an excellent reagent for detecting the presence of hypochlorous acid, and for ascertaining whether chlorine-water has been exposed to the rays of the sun; for in this case the protochloride of lead is instantly decomposed, and deposits pure oxide. From the preceding experiments we were led to seek whether the presence of the alkaline chlorides might not exercise upon the chloride of lead an analogous action to that which it has upon the protochloride of manganese. We found however that the reaction is very different.

Whenever a solution of chlorine in water containing one or several alkaline chlorides has not experienced the action of the direct rays of the sun, the protochloride of lead produces in it no precipitate of deutoxide. This metallic salt, which is very sparingly soluble and perfectly colourless, dissolves in the chlorinated liquid in pretty considerable proportion, and causes it to assume a very perceptible canary-yellow colour.

Make a cold saturated solution of chloride of sodium, then add to it a small quantity of protochloride of lead, and pass a current of washed chlorine into it; with the first bubbles of gas the yellow colour shows itself, and very different from that which chlorine produces on dissolving in water. By continuing the operation, the protochloride of lead is seen to dissolve, and disappears entirely, so that after some time a second and even a third dose may be added, which will dissolve wholly or in part, whilst the yellow colour of the liquid will become more and more deep, preserving nevertheless its canary-yellow tint. The absorption of the chlorine in this operation is very perceptible, contrary to what is known of the solubility of this gas in solutions of the alkaline chlorides. We finally arrive at a point when the solution of the protochloride of lead and the absorption of chlorine entirely ceases. The liquid may then be set aside, and decanted into bottles with ground stoppers, in which it keeps any length of time.

The following are the properties and reactions of this liquid:—It is of a deep yellow colour; its odour is that of a strong solution of chlorine; in a well-closed bottle it keeps very well, and is not altered by exposure to the direct rays of the sun. (It gives no precipitate of deutoxide of lead.) In an open vessel it loses its chlorine, and deposits protochloride of lead. If poured drop by drop into a large quantity of water, a precipitate is immediately obtained consisting of deutoxide of lead mixed with protochloride, in greater or less proportion according to the quantity of water employed.

When caustic alkali is added to the yellow liquid, deutoxide of lead is precipitated, which may be obtained in a very pure state by washing with hot water. Carbonate of lime produces in the yellow liquid a lively effervescence, with immediate precipitation of deutoxide of lead. Carbonate of potash causes a light brown precipitate,

the formation of which is not always accompanied by disengagement of carbonic acid. This precipitate is decomposed by washing and exposure to the air, its colour becomes darker, and it is converted into deutoxide of lead. It appears, therefore, that in this decomposition carbonate of deutoxide of lead is formed, a very unstable compound, which easily parts with its carbonic acid. Phosphate of soda likewise causes a light brown precipitate in the yellow liquid, which is probably phosphate of the deutoxide of lead, and which is not more stable than the carbonate, for simply washing it with cold water converts it into deutoxide.

If to the yellow liquid a little protochloride of manganese is added, a precipitate of deutoxide of manganese is obtained, as in chlorine solutions, mixed with alkaline chlorides; at the same time protochloride of lead separates.

The action of this yellow liquid upon the metals is very striking from its energy, which may be compared to that of *aqua regia*. Thus copper, iron, zinc, &c. are quickly attacked, and converted into chlorides, whilst protochloride of lead is precipitated; gold in thin leaves, platinum in the state of fine powder, quickly dissolve in it.

Organic substances are violently decomposed by contact with this liquid; they all precipitate protochloride of lead, furnishing products of their oxidation or chlorination. A solution of oxalic acid mixed with this yellow liquid immediately exhibits a lively effervescence, resulting from a very copious disengagement of carbonic acid.

Urea presents analogous phænomena. The salts of quinine and of morphine produce precipitates of a yellowish-white colour in the yellow solution, which are decomposed by washing with water, and converted into pure oxide.

What is the nature of the chlorinated compound of which we have sketched the history? The facts detailed lead us to think that the substance is a bichloride of lead of the formula $PbCl^2$, similar to the deutoxide PbO^2. This bichloride is however a very unstable compound, and is only formed in the presence of alkaline chlorides, with which it combines, probably acting the part of an acid. This very soluble compound cannot be isolated either by evaporation or by cooling. From the impossibility of analysing it in a pure state, we determined in the yellow liquid prepared with chloride of sodium the relative proportions of lead, chlorine and sodium. It is not probable that this latter metal is contained in the compound in any other state than that of chloride, NaCl; thus by subtracting from the total quantity of chlorine the amount required to saturate the sodium, we think that we have been able to determine with considerable approximation the relation between the lead and the chlorine. Our analyses have led us to numbers corresponding to the following composition:—

1 equiv. of lead.....	1294·0
$6\frac{1}{2}$ equivs. of chlorine	2879·5
$4\frac{1}{2}$ equivs. of sodium	1291·0

or, by doubling the number of equivalents, 2 equivs. lead, 13 equivs. chlorine, 9 equivs. sodium. Perhaps the formula of the double salt may be $2(PbCl^2)+9NaCl$?

We think therefore our experiments show that lead is capable of forming a bichloride corresponding to the binoxide, a new fact in the history of lead; and that this compound is formed in the presence of alkaline chlorides by the combination of chlorine with the protochloride.

We are also of opinion, that in preparing the brown oxide of lead for laboratory purposes, it will be frequently advantageous to use protochloride of lead mixed with a solution of chloride of sodium or other alkaline chloride saturated with chlorine, and then precipitating with an alkaline liquid, and washing the precipitate with much water. This method will at all events be quite as convenient in some circumstances as treating minium with nitric acid.—*Ann. de Chim.*, June 1850.

On a simple Process for demonstrating without danger the Liquefaction of Gases, and of Carbonic Acid in particular. By M. Berthelot.

Of late considerable attention has been paid to the liquefaction of gases by the employment of low temperatures and by pressure singly or combined. To produce without danger pressures having no other limits than those of the resistance of the vessels, I was led to use a method pointed out by the Academicians of Florence in their researches on the compressibility of water, and which is founded on the employment of the dilatation of a liquid as the means of pressure. The following is the method I have adopted:—I take some glass tubes of considerable thickness relatively to their bore; I close them at one end, fill them with pure dry mercury deprived of air, then draw them out so as to render them quite capillary at their open end, without diminishing the relation between the thickness and the internal diameter. I then heat the tube in a water-bath, its open point being immersed in a current of the gas which I want to compress. By the dilatation of the mercury a portion is expelled from the tube. When the temperature of the bath has reached 122° F., for instance, I gradually cool the tube to 32°. The mercury contracts, and the gas takes the place of the expelled mercury. I then withdraw the point from the current of gas, and immediately close it by sealing it at some millimetres from its aperture. The tube thus charged is replaced in the bath, which is again raised to 122°, then gradually higher, and the state of the gas observed in the capillary portion situated out of the bath at the ordinary temperature.

I have condensed in this manner chlorine and ammoniacal gas, the bath for the latter being at the temperature at which the mercury filled the tube, the chlorine slightly below it in a tube full of sulphuric acid. Carbonic acid in a tube full of mercury at 122° F., becomes liquid at 131°, the temperature of the bath, if the tube is very thick, otherwise at 138°, and at a lower temperature by pouring

a few drops of æther over the end. The liquefaction, repeated several times, once in the presence of M. Pelouze, was always complete. The portion which contained the liquid gas, produced when the bath was at 131°, was raised to 212°, the tube being heated to 136·4. At this moment the liquid occupied a volume more than double that which it had at the ordinary temperature, without exhibiting the least trace of vaporization. This enormous dilatability of liquid carbonic acid had already been pointed out by M. Thilorier.

These experiments are free from danger; the only precaution necessary is to have the tubes well drawn out; they then always burst in the widened part filled with mercury, which is accompanied by no projection or explosion. This method furnishes an easy means of showing on a small scale the liquefaction of gases. Barometer-tubes, somewhat strong, and the use of sulphuric acid in default of mercury, answer perfectly well.

I have tried to apply this method to those gases which have hitherto not been liquefied. For this purpose I filled three tubes, one with deutoxide of nitrogen, a second with carbonic oxide, and the last with oxygen; the tubes were filled with mercury at 122°, the bath raised to 140°; the first tube burst, while the two others did so at 158°. There was no trace of liquefaction perceptible. From the thickness of the tube containing the oxygen (external diameter 40 millimetres, internal diameter 3 millimetres), and the limits found by Messrs. Wertheim and Chevandier for the resistance until fracture of the kind of glass of which it was formed, this tube should not have burst below a pressure of about 780 atmospheres, a somewhat uncertain result notwithstanding the apparent homogeneity and the careful annealing of the material.

Perhaps by carrying the pressures nearly to the bursting of the glass, especially with the assistance of a powerful refrigeration, new results may be obtained by this method. I only once used solid carbonic acid, kindly furnished me by M. Deleuil. If the want of success of this method, which enables us to obtain almost indefinite pressures, should continue, we should probably conclude, as Mr. Faraday has already hinted, that pressure alone is not capable of effecting the liquefaction of gases under certain conditions of temperature.—*Comptes Rendus*, May 27, 1850.

On the Carbanilic Æthers of Alcohol and of Methylene. *By* G. Chancel.

In my researches on the nitrogenous compounds of the benzoic series*, I proved that nitrobenzamide is converted into carbanilamide, or anilamic urea, when it is treated with sulphuretted hydrogen or with hydrosulphate of ammonia. The new observations which form the subject of this notice prove that other bodies of the benzoic series may experience perfectly similar metamorphoses. Analogy, in fact, shows, that if nitrobenzamide furnishes carbanilamide under the influence of sulphuretted hydrogen, carbanilic æther ought to

* Chem. Gaz. vol. vii. p. 173.

be obtained by treating nitrobenzoic æther with the same reagent, for we have—

1st. $C^7 H^6 XNO + 3SH^2 = C^7 H^8 N^2 O + 2OH^2 + 3S$ *.
Nitrobenzamide. Carbanilamide.

2nd. $C^7 H^5 XO^2, C^2 H^4 + 3SH^2 = C^7 H^7 NO^2, C^2 H^4 + 2OH^2 + 3S$.
Nitrobenzoic æther. Carbanilic æther.

This was entirely confirmed by experiment. A body was obtained which was nothing less than urethane, in which the remainder of the ammonia is replaced by the remainder of the aniline. In order to indicate this analogy, I shall call the new substance obtained under these circumstances *carbanilethane*. Thus the molecular transformation, in virtue of which nitrobenzamide passes from the series (C^7) to the formic series (C) and phenic series (C^6), is completely reproduced with the nitrobenzoic æther of alcohol or of methylene.

Carbanilethane, or Carbanilic Æther of Alcohol.—To obtain this compound, it suffices to dissolve nitrobenzoic æther in alcohol, and to add a small quantity of hydrosulphate of ammonia; a copious deposit of sulphur is formed, and the reaction is soon completed when the mixture is placed on a moderately hot sand-bath. On the addition of water, an oily, heavy, and nearly colourless substance is precipitated, which is purified by redissolving it repeatedly in alcohol and precipitating it by water. The analysis of this compound led to the formula $C^9 H^{11} NO^2 = C^7 H^7 NO^2, C^2 H^4$, which is precisely that which theory assigns to carbanilethane.

The following reactions establish moreover in a positive manner the chemical functions of this substance. After a sufficient interval of time, the alcoholic solution, treated with potash, is no longer precipitated by water. If the alcohol is then expelled by ebullition, and some nitrate of silver added, a beautiful crop of crystals of carbanilate of silver is obtained on the cooling of the liquid. Thus, under the influence of potash, the new substance is entirely converted into carbanilate of potash and alcohol:—

$C^7 H^7 NO^2, C^2 H^4 + (KH)O = C^7 H^6 KNO^2 + C^2 H^6 O$.
Carbanilethane. Carbanilate of potash. Alcohol.

If ammonia is substituted for the potash, the carbanilethane is converted into alcohol and carbanilamide, which crystallizes on the spontaneous evaporation of the liquid:—

$C^7 H^7 NO^2, C^2 H^4 + H^3 N = C^7 H^8 N^2 O + C^2 H^6 O$.
Carbanilethane. Carbanilamide. Alcohol.

Carbanimethylane, or Carbanilic Æther of Methylene, is obtained by treating the nitrobenzoic æther of methylene with hydrosulphate of ammonia. It is likewise an oily substance, heavier than water. Its composition is expressed by the formula $C^8 H^9 NO^2 = C^7 H^7 NO^2, CH^2$. Its reactions are identical with those of its homologue of the ethylic series.—*Comptes Rendus*, June 10, 1850.

* $X = NO^2$, C = 12. H = 1, O = 16, N = 14.

On some new Facts relative to the Chemical Properties of Carbonic Oxide. *By* F. Leblanc.

In determining the amount of oxygen in a gas for illumination by means of the ammoniacal protochloride of copper, in company with MM. Stas and Doyère, we discovered a fact which had hitherto passed unnoticed, that the reagent in question dissolves a large quantity of carbonic oxide, and it even dissolves olefiant gas.

I undertook the investigation of this property, and the following are the results which I have obtained. When a current of carbonic oxide is passed into a solution of protochloride of copper in muriatic acid, the gas is absorbed in considerable quantity, equal to that of the absorption of carbonic acid by potash; the temperature however increases but little comparatively. The ammoniacal protochloride of copper, protected from contact with the air, behaves in the same way, and the quantity of gas absorbed is the same for the same quantity of copper in solution. This solution afterward turns blue in contact with the air, and may still be used to absorb oxygen.

The acid protochloride of copper, saturated with carbonic oxide may be diluted even largely with water without there being any precipitation of protochloride of copper, as before the absorption, and without disengagement of gas. Alcohol produces no turbidness, whilst æther appears to destroy the compound, at least partially. Hitherto I have not succeeded in obtaining the compound in the solid state, as I had expected from this reaction. Ebullition and exposure to a perfect vacuum expelled the gas; nevertheless I do not yet despair of isolating the compound.

The fact of the absorption of carbonic oxide by the protochloride of copper appears to belong to the same class as the absorption of the deutoxide of nitrogen by protosalts of iron, insofar as the absorption appears to take place in definite proportions. For the purpose of ascertaining this, I had to make use of a copper liquor of known strength, and to determine either the volume or the corresponding weight of the fixed carbonic oxide relatively to a certain quantity of copper. The numbers approach nearly to 1 equivalent of copper for 1 of carbonic oxide.

The protosalts of iron and tin have no action upon the carbonic oxide. The various salts of the protoxide of copper, dissolved in ammonia, for instance the sulphite, absorb carbonic oxide like the protochloride of copper.

These facts add, in my opinion, further interest to the chemical history of carbonic oxide, independently of furnishing a new test for carbonic oxide and the analysis of mixed gases; we find in it a fresh argument in favour of the hypothesis started some years ago by M. Dumas from the constitution and properties of chloroxycarbonic acid, and the presumed part acted by carbonic oxide in oxamide. According to this view, carbonic oxide would behave like a compound radical comparable in certain respects to cyanogen.

The absorption of carbonic oxide by potassium, to form a com-

pound containing the elements of condensed carbonic oxide, also favours this opinion, and establishes further analogy between carbonic oxide and cyanogen. I shall return to the question in a subsequent communication. In the mean time I have found that cyanogen is absorbed by the protochloride of copper, with formation of a chrome-yellow deposit, the colour of which changes rapidly by exposure to the air.—*Comptes Rendus*, April 22, 1850.

On the direct Production of Ethylamine, and on Alanine.
By Dr. Strecker.

When anhydrous sulphuric acid is passed into æther or alcohol, neutral sulphate of the oxide of ethyle is formed; and this is converted, on treatment with dry ammoniacal gas, into a crystalline ammonia salt of an acid, which contains the elements of sulphuric acid, alcohol and ethylamine. If the solution of this salt be precipitated with perchloride of platinum, only half the nitrogen separates in the form of the ammonio-chloride of platinum; and on evaporation the acid is decomposed, with elimination of ethylamine, which separates in combination with the excess of the perchloride of platinum in splendid golden scales.

I have also artificially prepared a new substance, resembling in many respects glycocoll and leucine. It will be remembered that Gerhardt and Laurent have asserted sarcosine, $C^6 H^7 NO^4$, to be homologous with glycocoll. This is not correct, as these substances have no resemblance to each other. I have discovered the member belonging to the glycocoll series, which is obtained in the following manner:—Prussic acid and aldehyde-ammonia are heated with muriatic acid, and from the evaporated residue ammonia and muriatic acid removed by boiling with hydrated oxide of lead, upon which the solution which contains much lead is treated with sulphuretted hydrogen. On evaporation, beautiful rhombic prisms of the new body, which I propose to call alanine, separate. Its formula is

$$C^2 NH + C^4 H^4 O^2 + 2HO = C^6 H^7 NO^4.$$

This is the fourth body now known which possesses this formula, viz. lactamide, urethane, sarcosine.

Alanine furnishes crystalline compounds both with bases (oxide of silver, oxide of lead, baryta) as well as with acids. It sublimes unaltered, and appears, like leucine, to form double salts with the nitrates. It also resembles leucine in many other respects, and we may perhaps expect to find it likewise as a product of decomposition of animal substances. It is my intention to extend this reaction to some other aldehydes, and I expect by the use of valerole ($C^{10} H^{10} O^2$) to obtain leucine. Unfortunately valerole is very difficult to obtain. —*Journ. für Prakt. Chem.*, May 15, 1850.

ANALYTICAL CHEMISTRY.

On a qualitative Test for Nitric Acid. *By* JAMES HIGGIN*.

THE methods in ordinary use of detecting nitric acid do not show very small quantities, and the liquid suspected to contain nitrates has generally to be concentrated before the presence of nitric acid can be ascertained.

Being engaged lately in testing for nitrates in water, I employed the following method with perfect success. It is founded on the immediate liberation of iodine from hydriodic acid by nitric acid, and its subsequent detection by starch.

To insure accuracy, certain minutiæ have to be attended to; and these observed, the test becomes one of great delicacy.

1. The solution of iodide of potassium must be very dilute, or iodine is liberated by sulphuric acid alone.

2. The solution of iodide of potassium must not be added to the mixture of sulphuric acid and liquid till cold, or iodine is apt to be liberated without the presence of nitric acid.

3. The proportion of sulphuric acid added to the suspected liquid must not be too great, or the most dilute solution of iodide of potassium gives iodine without nitric acid.

4. As the solution of hydriodic acid formed by the action of sulphuric acid upon iodide of potassium is decomposed by the air in the course of an hour or two, and a blue formed with starch, unless a distinct colour is produced in ten to fifteen minutes, it may be concluded that nitric acid is not present.

I dissolve 25 grs. of iodide of potassium in 16 oz. of water for the test solution, which is too dilute to give iodine with sulphuric acid alone.

To the suspected liquid in a test-tube I add not more than one-sixth of its bulk of concentrated sulphuric acid; heat nearly to a boil, and keep hot in the sand-bath for several minutes; cool the tube in cold water, and add a drop of starch-mucilage and a few drops of the test solution. If nitric acid is present, the liquid assumes a blue, very intense, with even $\frac{1}{300}$th part of nitric acid.

With	$\frac{1}{500}$th part by weight of NO^5,		intense dark blue.
...	$\frac{1}{1000}$th	...	dark blue.
...	$\frac{1}{5000}$th	...	dark blue.
...	$\frac{1}{10000}$th	...	paler blue.
...	$\frac{1}{12000}$th	...	pale blue.
..	$\frac{1}{16000}$th	...	blue tint.
...	$\frac{1}{18000}$th	..	blue tinge.
...	$\frac{1}{20000}$th	...	faint blue tinge, becoming decided in a few minutes.

It is remarkable that even with the great excess of sulphuric acid present the whole of the nitric acid is not liberated until after heating some time; thus $\frac{1}{16000}$th part required ten minutes heating before the test would indicate nitric acid; $\frac{1}{18000}$th I heated twenty minutes, and $\frac{1}{20000}$th I found necessary to heat half an hour before testing.

* Communicated by the Author.

Probably, by observing the same method, the other tests for nitric acid, viz. protosulphate of iron, sulphate of indigo and gold leaf, might become more delicate; but this I have not tried.

Of course some other acids would give the same results, as the chloric and chromic acids, &c.; but the absence of these is easily ascertained, and they occur seldom in analysis.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a direct Method of obtaining Iodine from certain Species of Sea-Weed on the large scale, with a Mode of procuring it as a subsidiary Product adapted to Coast Farms. By Geo. Kemp, M.D., *Cantab., Fellow of the Cambridge Philosophical Society*.*

The following paper contains the summary of a research on the above subject, made on the Isle of Man, at intervals, during the years 1847, 1848 and 1849; and, although distinguished by many district features, the principles involved are equally applicable to all localities similarly circumstanced. As a preliminary step, it may not be improper to remind the reader, that on all sea-coasts the marine vegetables may be classified according to the depths at which they are found; and for our present purpose it will merely be necessary to include them under two general classes, the shallow and deep water sea-weeds; the former of these embracing such growths as flourish between high and low water-marks, and the latter such as are only, or principally, found from low water-mark to the depth of three or four fathoms. We instance the *Fucus vesiculosus*, *F. serratus*, *F. nodosus* and *Halydrys siliquosa* as specimens of the first of these divisions; whilst the *Laminaria digitata*, *L. saccharina* and *L. bulbosa* will be sufficiently illustrative of the second, and have indeed furnished the principal materials for the investigation on which we are about to enter. It may further be premised, that nature, equally provident and fertile in her resources, seems to have destined these marine productions to act as her storehouses for the accumulation of certain inorganic bodies essential to terrestrial vegetation, and which, but for this provident care, would rapidly be out of human reach. In the Isle of Man this œconomical arrangement is peculiarly necessary. The more soluble portions of the granite, felspar, clay-schist, &c., which by attrition and solution are rapidly conveyed to the sea, are thus again presented to the agriculturist, and that in a condition admirably adapted for assimilation by the organs of plants; without this wise provision, he would be principally dependent for alkaline salts on masses of hard intractable rocks, the mechanical state of which would naturally form an almost insuperable barrier to the process of absorption. Referring to the excellent work of the Rev. J. G. Cumming for information on the

* Communicated by the Author.

geology and localities of the island, we now proceed to the principal chemical features of the two classes of sea-weed to which we have alluded; and it may be stated, as the general result of analysis, that the metallic base preponderating in the Fuci is sodium*, combined with oxysulphion, chlorine, and small quantities of iodine and bromine; whilst the plants which flourish in what Prof. E. Forbes has denominated the laminarian region are characterized by containing a preponderating quantity of potassium, with a far larger proportion of iodine than in the former species, and are on this account therefore of more interest and importance to the manufacturer. Many practical difficulties however prevent the maximum advantage to be derived from the above facts in a manufacturing point of view; and, in order to obviate them as much as possible, the writer was induced, at the commencement of his research, to apply to the Commissioners of Woods and Forests for permission to cut the sea-weed from the rocks, the preliminary object being to make comparative experiments on the particular period of growth at which these marine productions contain the largest amount of the element in question. Various circumstances, however, partly local, partly arising out of the nature of the case, rendered this formality unnecessary; it was, in fact, soon determined, that, in the earlier periods of growth, iodine is almost absent, progressing however with the advance of the plant, and at the maximum, at the precise period when the weed yields to the autumn tempests and is drifted on the shore, thus saving all the additional expense and risk of collecting from the rocks. Assuming then that two main points are established, viz. that the most fertile source of iodine is in the laminarian species, and in them at the period when their perennial functions are completed, we may allude to the present mode of obtaining the element from the ashes of the plant, which we shall designate the kelp process, and show how the assumed facts influence the operations of the manufacturer, or rather the impossibility of obtaining the maximum advantage derivable from a proper application of these facts with the present mode of extracting iodine by the kelp process. All sea-weed contains a very large proportion of sea-water; in the small shallow-water species this can be removed, by exposure in summer to the wind and sun, without great difficulty; in the other species, on the contrary, even under the most favourable circumstances, decomposition will occur before the plant can be brought into a condition favourable for its combustion; the consequence is, that the kelp process is principally confined to a species which contains but a small portion of iodine, and to a period of the year at which the other species has not arrived at maturity. The disadvantage does not rest here. The temperature, in forming kelp, cannot be so nicely controlled as to prevent the more volatile iodides being dissipated, or, what is of still more frequent occurrence, being lost

* Prof. Thomson states, on the authority of Gaultier de Claubry, that the *Fucus serratus* contains more iodine than *F. digitatus* or *vesiculosus*. The experience of the author is directly the reverse, presuming that the *F. digitatus* is identical with what is now denominated *Laminaria digitata*.

by mechanical agency, a very brisk current of hot air being set in motion by the very nature of the operation, accompanied as it usually is by a slight breeze. But another important point remains to be considered, which is indeed almost prohibitive of obtaining kelp rich in iodine in districts thickly inhabited. The smoke arising from the combustion of the *Laminaria digitata* particularly is most offensive; and, unless the wind is blowing off shore, the burning the weed on the large scale would be probibited, or the party who undertakes the process be constantly engaged in law proceedings; and as the laws in the Isle of Man are either peculiar or peculiarly administered, no reasonable prospect could be entertained of ultimate success. All these circumstances, taken collectively, induced the writer to seek out a method by which these evils might be obviated; and in doing so it became necessary to determine in what portion of the plant the element sought after is contained in greatest abundance, and whether it would not be practicable by mechanical means to arrive at the desired result. Excluding then for the future the shallow-water species, we confine our remarks to the modes pursued with reference to the *Laminaria digitata* and *L. saccharina*, principally indeed to the first, as it not only presented the greater difficulty, but also was furnished in greater abundance.

On making then a transverse section of the stem of the *L. digitata*, we observe externally a thin cortical layer, next a mass of condensed cellular tissue, and internally a transparent medullary central portion, generally of an elliptical form. Applying to one of these surfaces a weak solution either of acetic or hydrochloric acid, we cover it with a very slight layer of starch-paste, and cautiously expose it to the action of chlorine, from the mouth of a bottle containing a solution of that gas. The iodine being set free, and rendering its presence perceptible through combination with amylon, will be immediately proved to be enveloped in cells between the external cortical and central medullary portions. An important step has now been made in the investigation, and hopes were at first entertained that the object sought after would at once be arrived at, by exposing the stem of the plant to pressure and from the liquid obtained, which it was presumed would contain the greater portion of iodides in solution, without further trouble liberating the iodine itself. Great physical difficulties however presented themselves; and so condensed was the cellular tissue found, that on exposing a portion, not exceeding the dimensions of a cubic inch, to the pressure of a ton weight, but a very small portion of fluid was obtained, although Professor Forchhammer* estimates this at 75 per cent., a quantity far less than has been found at different times by my friend Mr. Waldie of Liverpool and myself. It was determined, therefore, in the next experiment, to break up the cellular tissue as completely

* "At the point of Kronborg, near Elsingor, about 30,000 two-horse loads of sea-weed are annually thrown on shore in the months of November and December, which, calculated at 500 lbs. dry plants each, are equal to 15 millions of pounds."—Forchhammer *on the Metamorphosed Fucoid Schists in Scandinavia*; *Report of British Association for* 1844, p. 163.

as possible, by rubbing the stem on an ordinary domestic grater. The result was perfectly satisfactory, and the iodine liberated, by ordinary chemical operations, with the greatest ease; but it was necessary to modify the plan, so as to adapt it for application on a large scale. A turnip-cutter was therefore furnished with a small band-wheel of 6 inches in diameter, and this connected by means of a band with a wheel 5 feet in diameter, which in working was caused to revolve eighty times per minute, thus communicating to the smaller wheel a velocity of 800 revolutions per minute; and the machine being supplied with the stem divested of roots and terminal leaves, it was cut into small slices with great rapidity. The original intention was to pass these slices through another machine, prepared for the purpose, which would have reduced these slices to a pulp, thus effectually breaking up the cellular tissue, and then proceeding to express the fluid, and liberate the iodine as in the type experiment. Nature however interposed to save the trouble, for the mass of slices having been left in a heap for about twelve hours, a species of fermentation commenced, with evolution of heat and other phænomena, which reduced the whole mass to a pulp without further trouble; and this mass being submitted to adequate pressure, completed the object in view. The fibrous tissue left in the press still contains iodine; but the pressed mass is so easily charred at a low temperature, that on a large scale this method will no doubt be preferred to the more circuitous course.

With reference to the *Laminaria saccharina*, which in the autumn is very rich in iodine, the plan of extraction is still simpler. Having collected this, as drift-weed, it is only necessary to heap it up in vats, or other receptacles of adequate size, with a tap at the bottom to allow the liquid to escape. For some hours nothing but sea-water runs off; at a certain stage, however, and time, mainly dependent upon quantity and temperature, active fermentation sets in; and as it is presumed that the liquid running off is carefully tested for iodine from time to time, immediately its appearance is indicated the tap should be closed, and during the next twelve hours the contents of the vat should be occasionally moved or stirred about. When the contents have been reduced to a soft pultaceous magma, in which all remaining cellular tissue can be readily broken down by the hand, the addition of quicklime in sufficient quantities, which will vary with the amount of substance operated upon, but may easily be determined by experience, completes the process; and in this case almost the whole of the iodides in solution may be removed by expression. In localities where lime is expensive, the process of charring may be resorted to.

The subsequent steps of the operation will be much influenced by circumstances. If the object be merely to save the iodine, a variety of methods may be adopted to effect this purpose, one of which will be mentioned in the sequel; if, on the other hand, it be a consideration to obtain the potash salts, evaporation, and probably repeated crystallizations, must be resorted to; and the facility of obtaining fuel at little expense will of course become an important

element for consideration. It will however at once occur, that the cellular tissue which remains after pressure will render important service in this case; at all events, but little experience and ingenuity will be called into requisition for combining all the favourable circumstances in such a manner as to ensure a profitable arrangement. Whilst the use of iodine remains a matter of importance only in a pharmaceutical point of view, the demand must necessarily be limited; and such a supply as could easily be obtained by the above method would materially affect the market; but should any means be discovered of rendering it adapted to the purposes of dyeing, the application of sufficient capital would doubtless be attended with very profitable results.

Another case presents itself, in which a modification of the above plan, carried out on a limited scale, may be of extensive practical benefit. On all coasts similarly circumstanced with that to which we more especially allude, numerous creeks occur, which for the most part either belong to farms in their immediate neighbourhood, or do so virtually, as access to them can only be obtained by a right of way through such farms; in these, immense quantities of drift-weed accumulate after every storm, which in many cases are entirely wasted, and in many others have to be conveyed to the land by roads almost impassable. Now it will be seen in the sequel, that, by a little attention, the agriculturist may convert these natural disadvantages into sources of profit; on the one hand, eliminating an important element, which under ordinary circumstances is entirely lost; on the other, reducing all that is valuable for farm purposes into a concentrated form, admitting of transit with great œconomy of labour and expense. Taking Professor Forchhammer's estimate, that each ton of sea-weed is reduced by drying to 500 lbs. of solid matter (and, so far as the writer's experience is concerned, this estimate is far above the mark), in every ton of *wrack* conveyed to the land, the farmer actually carts away, and that sometimes for miles, 1740 lbs. of water, which is all but lost labour, his object being merely to supply his land with the salts of potash and soda. By pursuing the following method, not only may a large saving be effected, but in many small holdings intelligence and industry may, from the sea-weed alone, secure a greater return than the whole produce of the farm taken collectively. It is now the writer's object to project a plan for the accomplishment of this result; but it will be previously necessary to make a slight digression.

The mutual reaction of free iodine and starch is well known; but little attention has hitherto been bestowed on the circumstance, that the facility with which iodine is precipitated from its solutions by means of starch varies exceedingly. The object of the writer being to fall on some plan, involving little expense and chemical knowledge, to effect the complete precipitation of free iodine from its solutions, he was led to the more minute investigation of the subject in detail; and, in the first place, it was found out, that the facility with which the iodide of amylon was precipitated depends in a great measure on the size of the starch-granule. This would lead one to

suppose that the vesicular covering of the granule is the substance which more immediately combines with the iodine, or that the solution of iodine enters the vesicle by means of endosmose; in either case the practical result will be the same. Now, according to Raspail's observations, the granule of millet-starch is only $\frac{1}{10000}$th, that of wheat $\frac{1}{500}$th, whilst that of the potato is $\frac{1}{200}$th of an inch in diameter. By taking advantage of this observation, even considering it as a mere approximation (for the granules of the same species vary exceedingly in size), the facility of precipitation is much increased, favoured as we are by the additional circumstance, that this is the very species of starch which may be obtained at the least, and in fact almost nominal cost. But, further, by adding a solution of ammonia to a solution of the neutral acetate of lead, we obtain, as is well known, the tribasic acetate of lead, $PbO(C^4H^3O^3)+2PbO$. By adding a solution of this compound to starch, we form an insoluble compound of starch with oxide of lead; and by making use of this substance, which can be obtained with great facility and at a trifling expense, we can in a few seconds precipitate any quantity of iodine from a solution; by taking advantage also of the weight and denseness of the precipitate, we can decant the supernatant liquid, and if necessary repeatedly wash the precipitate without loss. A few precautions will still better adapt the above plan to the end designed, and facilitate manipulations considerably. Let the potato-starch be formed as usual, by grating and washing, and then strained through a sieve or coarse linen, to separate it from the broken-down cellular tissue; the turbid liquid should now be allowed to repose for a few minutes, and the supernatant milky fluid be poured off; the residuum is again washed, and treated in the same manner, until the precipitate subsides rapidly, and the liquid clears in a few seconds; the smaller granules are thus removed. Having previously prepared a strong solution of acetate of lead, with the addition of caustic ammonia, this is now added, and the compound sought after immediately prepared, which is then ready for use, or may be strained through flannel, dried, and kept ready for application.

We now revert to the course which we propose for the adoption of the agriculturist.

The sea-weed being collected in heaps, may be suffered to drain itself of the sea-water mechanically retained about it. As this will occupy some hours, the time may be employed by women and children in trimming the stalks of the tangle (*Laminaria digitata*) of leaves and roots, and arranging them ready for the turnip-cutter and other operations, as stated above. The whole of the remainder may then be conveyed into old hogsheads, in a sheltered spot near the beach, and allowed to ferment; the succeeding operations having already been described. A quantity of liquid is now assumed to have been collected, to which is added commercial hydrochloric acid, until a very marked acid reaction is obtained; a solution of ordinary chlorinated lime is then added, to disengage the iodine, taking especial care not to use an excess. A very little practice will decide the quantity necessary, as the brown colour of the liquid

will increase up to a certain point, and the smallest addition of chlorine, when this has been attained, will diminish its intensity. Having thus liberated the iodine, it is precipitated with the prepared starch diffused through water, continuing its addition until it is no longer rendered blue by the iodine. The remainder of the process consists in decanting the fluid portion, and straining the residuum, which when dry will be immediately available to the iodine manufacturer, and from which the iodide of potassium may be formed by the addition of sulphuret of potassium, or other appropriate means. The fluid portion being rich in potash, soda and magnesian salts, will form a most important contribution to the liquid manure-tank, or may be thrown over the compost in the farm-yard, with the additional advantage of fixing the ammonia through its excess of hydrochloric acid. The cakes of cellular tissue should be stored in a dry place, and made use of as fuel for steaming turnips, and other similar operations, taking care to preserve the ashes; these should also be lixiviated, and thus every particle of iodine may be saved.

Such is a general outline of the writer's plan. In a journal nothing more can be given; but those who are interested in the matter will find little difficulty in expanding these views, or adapting them to special purposes.

Caernarvon, North Wales,
June 5th, 1850.

On an improved Process for manufacturing Chlorate of Potash. *By* F. C. Calvert.

My attention having been directed to the chlorates, the many and useful applications which might be made of them were their high price not opposed to their commercial use, I have sought to discover a less expensive mode of preparation. I think I have succeeded with regard to the chlorate of potash, and will now submit the results of my experiments.

The first chlorates which I obtained were those of lime and baryta. I easily produced them by passing a current of chlorine into the milks of lime and carbonate of baryta at a boiling, and not at the ordinary temperature; for in the latter case, as is well known, only hypochlorites are obtained. The difficulty of separating the chlorites of baryta and lime from the chlorides of these metals caused me to give up their preparation on a large scale.

I then tried to discover a more simple method of preparing the chlorate of potash, and arrived at this result by an entirely new chemical reaction, *i. e.* by forming a mixture of $5\frac{1}{2}$ equivs. of burnt lime for 1 equiv. caustic potash, and passing a current of chlorine through the hot mixture. Under these conditions chloride of calcium and chlorate of potash are produced. Thus, by the use of lime, the enormous loss of potash, which in the ordinary process is converted into chloride, is avoided; since, instead of producing 43 grs. for 100 grs. of potash, I obtained 220 grs., which approaches very closely to the theoretical number, 260.

A fact which demonstrates in a remarkable manner how greatly

the chemical affinity of chlorine for oxygen is increased by heat is, that a mere trace of chlorate is produced when chlorine is passed into a mixture of lime and caustic potash at the ordinary temperature.

Another point which results from my experiments is, the influence of the degree of concentration of the liquids. If, for instance, a solution of caustic potash, of 1·040 spec. grav., at 82°, and containing 34 grs. of potash in 1000 grs. of liquid, is mixed with 431 grs. of lime, or 6 equivs., only 131 grs. of chlorate are obtained. Another mixture, made with 1000 grs. of liquid containing 58·75 of potash and 6 equivs. of lime, gave 158 grs. of chlorate of potash. Lastly, by taking a solution of caustic potash of 1·110 spec. grav., and containing 102·33 of potash for 100 grs. of fluid, and adding to it 6 equivs. of caustic lime, heating the whole gradually to 122°, then passing a rapid current of chlorine to saturation (which raises the temperature to about 194°), filtering, evaporating to dryness, redissolving in boiling water, and allowing the whole to cool, I obtained 220 grs. of pure chlorate of potash. This process has been applied on a large scale, and has perfectly succeeded.—*Comptes Rendus*, May 27, 1850.

Process of Engraving upon Ivory.

The process used to cover ivory with ornaments and designs in black consists in engraving in the ivory itself, and then filling in the designs with a black hard varnish.

To obtain finer and more regular designs, the ivory is to be covered with the common ground, and by means of the point the designs are engraved upon it. They are then eaten in by a solution formed as follows:—

Fine silver	6 grms.
Nitric acid	30 ...
Distilled water	125 ...

At the end of about a half-hour, according to the depth to be given, it is to be washed with distilled water and dried with bibulous paper. The design is then exposed for an hour to the solar light, and the layer of wax is removed by essence of turpentine.

The design has then a black colour or a dark brown, which blackens entirely at the end of one or two days. Other colours may be produced, by replacing the solution of nitrate of silver by a solution of gold or platina in *aqua regia* or of copper in nitric acid. *Revue Scientifique*, xxxv. p. 433.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

May 20, 1850. (Robert Porrett, Esq., in the Chair.) The following papers were read:—

"On Chlorophosphuret of Nitrogen, and its Products of Decomposition," by J. H. Gladstone, Ph.D.

The author's method of preparing chlorophosphuret of nitrogen consists in heating, in a florence flask, 1 part of pentachloride of phosphorus and 2 parts of well-dried chloride of ammonium. The products of the action are oxychloride of phosphorus, $PCl^3 O^2$ (due to the accidental presence of moisture), hydrochloric acid and the chlorophosphuret, the bulk of which remains in the flask. It may be purified either by dissolving it in æther or by boiling it in water, which does not dissolve it. The purified substance is solid and crystalline, melts at 110° C., and boils at 240° C. The analysis of the author confirms the formula of Liebig and Wöhler, $P^3 N^2 Cl^5$.

When dissolved in an alcoholic solution of potash or ammonia, the chlorophosphuret is decomposed, and the solution, after evaporation to dryness and resolution in water, contains an acid, which the author calls azophosphoric acid. The principal characteristic of the acid is, that, boiled even with an acid solution of a salt of sesquioxide of iron, a white precipitate is formed. For this precipitate, dried at a temperature not lower than 100° C., the analysis led to the formula $Fe^2 O^3, P^2 NO^5, 4HO$; dried at 70° C., the salt contains 5 atoms of water. The salts of copper, silver and baryta are all tribasic. The acid itself, a semifluid crystalline substance, was obtained by decomposing the silver salt by hydrochloric acid.

"On the Action of Chloride of Cyanogen on Toluidine," by W. Wilson.

Toluol was prepared by the author from coal-tar naphtha, and converted into nitrotoluol in the usual manner. The conversion into toluidine was effected by distillation with hydrosulphate of sulphide of potassium (instead of the sulphide of ammonium), in which way the change is effected in half the usual time. By the action of chloride of cyanogen on the toluidine, the hydrochlorate of a new base is formed, which the author calls metatoluidine. Its constitution was determined by the analysis of the base itself and of the platinum salt, which gave for it the formula $C^{30} H^{17} N^3 = 2$ equivs. of toluidine + 1 equiv. of chloride of cyanogen.

"On the Identity of Bisulphamylic and Hyposulphamylic Acids," by Joseph Danson.

The hyposulphamylic acid was prepared by the action of nitric acid on the bisulphide of amyle; nitrogen and the oxides of nitrogen are evolved during the action. After purification, a colourless oily fluid was obtained, which is the pure hyposulphamylic acid. The author analysed the baryta salt, to which his analyses give the formula $BaO, C^{10} H^{11} S^2 O^5$; and hence he concludes that this acid is identical with that procured by the action of nitric acid upon the sulphocyanide of amyle, to which the analyses of Gerathwohl give one more equiv. of hydrogen.

Society of Arts.

May 1, 1850. The following paper was read:—

"On the Causes and Preventives of Mildew in Paper and Parchments, with an account of Experiments made on the Saturation of

growing Wood with Antiseptic Chemical Solutions," by Alfred Gyde, Esq., M.R.C.S.E.*

The author stated, that, owing to the imperfections formerly existing in the microscope, little was known of the real nature of the class of plants called *fungi* until within the last few years; but, since the improvements in that instrument, the subject of the development, growth and offices of the fungi has received much attention. They compose, with the algæ and lichens, the class of thallogens (Lindley), the algæ existing in water, the other two in air only. A fungus is a cellular flowerless plant, fructifying solely by spores, by which it is propagated, and the methods of attachment of which are singularly various and beautiful. The fungi differ from the lichens and algæ in deriving their nourishment from the substances on which they grow, instead of from the media in which they live. They contain a larger quantity of nitrogen in their constitution than vegetables in general do, and the substance called "fungine" has a near resemblance to animal matter. Their spores are inconceivably numerous and minute, and are diffused very widely, developing themselves wherever they find organic matter in a fit state. The principal conditions required for their growth are moisture, heat, and the presence of oxygen and of electricity. No decomposition or development of fungi takes place in dry organic matter; a fact illustrated by the high state of preservation in which timber has been found after the lapse of centuries, as well as by the condition of mummy-cases, bandages, &c., kept dry in the hot climate of Egypt. Decay will not take place in a temperature below that of the freezing-point of water, nor without oxygen; by excluding which, as contained in the air, meat and vegetables may be kept fresh and sweet for many years.

The action which takes place when moist vegetable substances are exposed to oxygen is that of slow combustion (it has been called by Liebig "eremacausis"); the oxygen uniting with the wood and liberating a volume equal to itself of carbonic acid, and another portion combining with the hydrogen of the wood to form water. Decomposition takes place on contact with a body already undergoing the same change, in the same manner that yeast causes fermentation. Animal matter enters into combination with oxygen in precisely the same way with vegetable matter; but as, in addition to carbon and hydrogen, it contains nitrogen, the products of the eremacausis are more numerous—carbon and nitrate of ammonia, carburetted and sulphuretted hydrogen and water; and these ammoniacal salts greatly favour the growth of fungi. Now paper consists essentially of woody fibre, having animal matter as size on its surface.

The first microscopic symptom of decay in paper is irregularity of surface, with slight change of colour, indicating the commencement of the processes just noticed; during which, in addition to carbonic acid, certain organic acids are formed, as crenic and ulmic acids, which, if the paper has been stained by a colouring matter,

* This paper was rewarded, in 1848, with the Society's gold Isis medal.

will form spots of red on the surface. Spots of the same kind are similarly formed on leather coloured during its manufacture. Provided that fungi have not taken root, the colour can be restored by ammonia or any alkali. The same process of decay goes on in parchment as in paper, only with more rapidity, from the presence of nitrogen in its composition. When this decay has begun to take place, fungi are produced, the most common species being *Penicilium glaucum*. They insinuate themselves between the fibre, causing a freer admission of air, and consequently hasten the decay.

The substances most successfully used as preventives of decay are the salts of mercury, copper and zinc. Bichloride of mercury (corrosive sublimate) is the material employed in the kyanization of timber, the probable mode of action being its combination with the albumen of the wood, to form an insoluble compound insusceptible of spontaneous decomposition, and therefore incapable of exciting fermentation. The antiseptic power of corrosive sublimate may be easily tested by mixing a little of it with flour-paste, the decay of and appearance of fungi on which are quite prevented by it. Next to corrosive sublimate, in antiseptic value, stand the salts of copper and zinc. Chloride of zinc has been patented by Sir W. Burnett for the preservation of wood, sail-cloth, &c., and appears to succeed admirably. For use in the preservation of paper, the sulphate of zinc is better than the chloride, which is to a certain extent deliquescent.

A series of experiments were made, in the summer of 1840, on the use of metallic and other solutions for the preservation of wood. A deep saw-cut was made all round the circumference of some growing trees near their base, into which the solutions were introduced by forming a basin of clay beneath the cut; thus the solution took the place of the ascending sap, and in periods of time varying from one to three days was found to have impregnated even the topmost leaves of trees fifty feet high. The trees were chiefly beech and larch. After impregnation they were felled, and specimens about five feet long by two inches square were cut out, and packed in decaying sawdust in a warm damp cellar, where they were left for seven years. The details of the experiment are given in a table, by which the following general results are made to appear:—The pieces of wood saturated with sulphate of copper in the proportion of one pound to one gallon of water, or with acetate of copper in the proportion of one pound to one pint of vinegar and one gallon of water, were found in perfect preservation, clean, dry and free from fungus; but the remaining pieces, which were saturated with nitrate of soda, prussiate of potash, acetate of iron, sulphate of iron, common salt and kreosote, presented much decay and a large growth of fungi.

The results obtained from solutions of corrosive sublimate, one-eighteenth of a pound to a gallon of water (Kyan's proportion), varied in an anomalous manner.

The paper was accompanied by specimens of the wood, showing how complete had been the saturation.

THE CHEMICAL GAZETTE.

No. CLXXXVI.—July 15, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Nutrition of Plants. By Prof. Magnus.

Prof. Magnus has instituted a series of experiments upon the vegetation of barley. The barley was subjected essentially to the same treatment as that adopted by the Prince of Salm Horstmar; in the analyses, the results of all those experiments which have been made in recent times have been applied.

The author preferred this method of determining the constituents necessary for the growth of the barley to that of the mere ash analyses, for the reason, that although the latter enable us to ascertain what inorganic constituents occur in a plant, they do not give us any further information as to whether they are all requisite for it. If the latter were the case, the ashes of the same species of plant ought always to exhibit the same composition, whilst in fact rather considerable deviations occur. This evidently depends upon the circumstance, that sometimes more, sometimes less of the alkalies and earths contained in the soil enter the juices of the plants, according as they exist in a more or less soluble state, as Saussure has already shown by his experiments.

On drying the plants, the mineral constituents contained in the juice, which are thus as it were accidental ingredients, are left, and are subsequently met with in the ash. Hence this sometimes amounts to more, sometimes to less; and contains sometimes more of one, sometimes more of another inorganic substance, according as this has been supplied to it from the soil. Hence it is possible that certain substances, which are by no means essential to the existence of a plant, may constantly be met with in its ash. We might imagine, *e. g.* that the lime or magnesia which occur in all manures, and are therefore met with in all ashes, are still by no means indispensably requisite for some plants. We must therefore enter upon a synthetical method, in addition to the analytical one which has hitherto been adopted. With this view Prof. Magnus placed grains of barley in pure carbonized sugar in a series of experiments; various salts were then added to this; and in another series of experiments, the same seeds were placed in pure felspar. The carbon was obtained from pure white sugar-candy, which was fused in a large porcelain dish, and heated until it formed a hard mass; this was then taken from it, and thoroughly heated to redness in a well-closed porcelain crucible. To be certain that the carbon contained no mineral consti-

tuents, 2 grms. of it were burnt upon silver foil in oxygen gas. They left a mere trace of residue, which weighed much less than $\frac{1}{2}$ a milligramme, hence less than $\frac{1}{1000}$th of the weight of the carbon. Eight different experiments were made with this carbon. In one, it was used without any addition; in the second, all the mineral matters existing in the plants were mixed with it, and in the following quantities:—

	per cent. of the weight of the carbon.
Carbonate of lime	4·0
Protocarbonate of manganese	0·5
Carbonate of magnesia	2·0
Peroxide of iron	1·0
Sulphate of lime	1·0
Phosphate of lime	2·0
Chloride of sodium	0·5
Chloride of potassium	0·5
Silicate of potash (soluble glass)	4·0
	15·5

In the third, all these salts, with the exception of the silicate of potash, were added to the carbon, being most intimately mixed with it, as in all the following experiments; the silicic acid was therefore absent. In the fourth, the chloride of sodium was omitted instead of the former; sodium was therefore absent. In the fifth, the phosphate of lime was omitted; phosphoric acid was therefore wanting. In the sixth, the sulphate of lime; hence there was no sulphuric acid. In the seventh, the protocarbonate of manganese; and to be certain that the peroxide of iron used in this experiment was perfectly free from manganese, it had been precipitated by succinate of ammonia; hence there was no manganese present. In the eighth, the chloride of potassium and the silicate of potash were omitted; and instead of them, 1·5 per cent. of finely-powdered and elutriated rock-crystal were added; here potash was therefore absent.

In each of these experiments, three different vessels were used; in each of them a grain of barley was placed, so that each experiment was performed three times. The vessels were made of zinc, coated with a thick layer of rosin and wax. Their diameter at the top was 1·75, at the bottom 0·5 inch, and they were 5 inches in height. To avoid the variations of temperature, which readily occur in such small vessels, there were always twelve of them fitted into the lid of a wooden box containing sand, so that the zinc vessels were perfectly surrounded with sand.

These boxes were placed in a front window of a room facing the south. By opening small panes, the air could be sufficiently renewed. Although the deposition of dust could not be entirely avoided in this way, yet it was as little as possible in experiments of this kind. As often as the carbon got dry, it was moistened with distilled water; and to restore the deficient nitrogen to the plants, water containing one-thousandth of its weight of carbonate of ammonia was added, a quantity which is imperceptible to the tongue.

In those vessels which contained carbon without any addition, the plants attained a height of 5 inches. In the others they were either stunted or undeveloped. As in the latter an effervescence of a white salt almost invariably appeared upon the surface of the carbon, this gave rise to the supposition that the carbon might have contained too large a quantity of soluble salts. To remove these, the plants were taken out of the carbon, and then each of the seven mixtures mentioned above, with which the experiments 2 to 8 inclusive had been made, were exhausted with water. Three new vessels were then filled with each of them, and two grains of barley placed in each vessel.

The plants then developed were unequally strong, and in some of these mixtures they even attained a height of 14 inches, whilst those in the vessels containing the pure carbon became developed to a height of 5 inches only. Hence it is evident that the presence of even a small quantity of salts is injurious to vegetation. At first, salts to the amount of 15·5 per cent. of the weight of the carbon were added; of these, however, the chloride of sodium and chloride of potassium were the only soluble ones, and these together do not form more than 1 per cent., and very small quantities only of difficultly-soluble salts, as sulphate of lime, were present. Scarcely any development then took place; but after the greater portion of these had been removed by exhaustion with water, the plants grew better, although, even after this treatment, the quantity of the remaining salts appeared still too great. The experiment however showed decidedly that barley cannot be developed without some mineral matter, but dies after having attained a height of 5 inches; whilst, when a small quantity of salts is added, vegetation proceeds much further. How far it would be possible, however, so to mix the small quantities of the various salts with the carbon, that they may be uniformly distributed, and that perfect development of the plants be attained, can only be decided by subsequent investigations. In other similar experiments, also, which the author made, the injurious influence of salts was equally distinctly perceptible. Thus, instead of the carbon, a coarsely-powdered felspar, which occurs at Silesia near the Schreibersau, and is used at the porcelain manufactory of Berlin, was employed. It had been powdered at this manufactory by an iron stamp. Part of it was used in a pure state; to another part all the above-mentioned salts were applied, and of these to 100 parts of felspar—

	per cent.
Carbonate of lime	2·0
Carbonate of magnesia	2·0
Protocarbonate of manganese	0·5
Sulphate of lime	1·0
Phosphate of lime	2·0
Chloride of sodium	0·5
Silicate of potash	1·0
Spathic iron ore	1·0
	10·0

The spathic iron, from its insolubility in aqueous solution of carbonic acid, appeared better adapted for experiments upon vegetation than peroxide of iron which has been heated to redness, for this is perfectly insoluble. That used in these experiments came from Lobenstein, and according to an analysis by Hagen contained—

	per cent.
Protoxide of iron	45·79
Protoxide of manganese	11·34
Lime	1·08
Magnesia	3·25
Carbonic acid	39·27
	100·73

An experiment was also made, in which the same salts, with the exception of the phosphate of lime, as well as a third, in which all the salts, with the exception of the silicate of potash, were mixed with the felspar. Three small porcelain pots were filled with these three mixtures, and three or four grains of barley placed in each; water was then poured over them. The grains however did not spring up.

The three spoiled grains were then removed, and each of the three mixtures exhausted with distilled water. When three porcelain pots were now again filled, and the grains of barley placed in each, the plants in all the three mixtures attained on an average a height of 14 inches, and sent forth, some five, others seven leaves.

Besides these mixtures, some grains of barley were also placed in pure felspar. They attained a height of 15 inches, and produced seven perfect leaves. All the plants then produced ears, and one of them brought forth two perfectly-developed grains; whilst in all the other experiments, both with carbon and felspar, no trace of ear was apparent. The plants produced in the pure felspar also were of such strength, that even after the lower leaves had perfectly withered, new shoots were sent out from at least two of them.

A perfectly similar result was yielded by an experiment in which the same felspar was used, a third part of which however had been ground fine and elubriated, the same substance from the porcelain manufactory being again made use of. In this case, one plant attained a height of 20 inches, and produced four perfect grains. The plants in this finely-granular mass were altogether stronger than those in the coarse felspar, but their first evolution occupied a much longer time than in the latter.

The two latter experiments show the great influence of the mechanical structure of the soil upon vegetation. In both, the same felspar was used; both were begun at the same time, and carried out under exactly similar circumstances; but the progress of vegetation in the two was totally different. In the coarsely-powdered felspar, the grains had all sprung up at the end of five days; whilst in the fine, they required eight days. For the latter had become so hard and solid by being moistened with water, that a hole could hardly be bored in it with a pointed iron; it was therefore natural that the

leaf-bud which was formed could scarcely force its way through it. But when the plants had attained a height of 5 inches, those in the fine felspar appeared much stronger, and surpassed the former in their vegetation. This probably arose from the circumstance, that the finer mass retains moisture better, and absorbs carbonic acid and ammonia from the atmosphere in larger quantities. Moreover, it might also happen that the felspar was partially decomposed, and that this decomposition took place more easily in the case of the fine than the coarse. But that the vegetation took place so much better altogether in the pure felspar than in that treated with salts, even when the soluble portion of the latter was removed by exhaustion with water, affords proof of the small quantities of salts required by the plants for their nutrition, and how injurious is the presence of larger quantities.

In addition to these experiments, which in the advanced autumnal state of the season were necessarily interrupted, the author has also endeavoured to ascertain by experiments, how far the vegetable and animal refuse, which is added to the soil to increase its fertility, effects this by the mineral matters which it contains only, or whether the organic constituents also play an essential part in it. He set out with the consideration, that if a soil upon which it is known that a particular plant is capable of becoming perfectly developed, is in a condition to bring forth the same plant of equal strength after all the organic constituents which it contained have been completely removed, this would be a proof that the latter exert no influence upon vegetation.

For the purpose of determining how far this is the case, a quantity of soil, which according to the statement of the owner was adapted to the cultivation of barley without further manuring, was heated in a covered crucible to perfect redness, and retained in this state for an hour. On cooling, the mass was of a black colour, from the carbon left on the decomposition of the organic constituents.

To remove this, a portion of this black earth was heated in a current of oxygen until it contained no more combustible matter. After having been heated to redness in the oxygen, the earth was of a red colour. Some barley was placed both in the earth which had not, as also in that which had been heated to redness and still contained carbon, as also in that which had been perfectly freed from all organic constituents, each being placed in a porcelain or glass vessel. The season of the year was somewhat advanced, for this was done in the month of June; but the plants sprang up rapidly, and became developed in all the three vessels in exactly the same manner. After a period of growth of about ten weeks' duration, they attained a height of somewhat more than 15 inches, and all were furnished with ears, which however did not contain more than four perfectly-developed grains.

It is evident, from this uniform development, that the small quantities of organic remains existing in the ordinary soil, when not recently manured, exert scarcely any perceptible influence upon vegetation. For the sake of comparison, some of the same barley was

simultaneously placed in some garden soil which had been manured the preceding year; it was kept in a porcelain flower-pot, which was placed near those mentioned in the preceding experiment. In this earth the vegetation was more vigorous, and the hulm much stronger than in the common soil. The plants certainly did not attain a greater height than in the former, and the ears contained only five grains; but the entire plant was much more foliaceous and luxuriant. Possibly the garden soil contained the mineral ingredients required by the barley in a more readily assimilable form than the common soil, and this was the cause of its great fertility; still the idea urges itself upon us, that the organic substances it contains cannot have remained without influence. To determine accurately if and how far this has been the case, the author endeavoured to manure the soil without bringing the manure into contact with it, hence in such a manner that this could only exert its action at a distance. For this purpose, a quantity of the common soil, which had been heated in a current of oxygen, was introduced into a glass, which was placed in a zinc vessel, and the latter hermetically closed by a tall bell-glass, eight grains of barley having been previously placed in the soil. Beneath the bell-glass, but separated from the soil, was a quantity of freshly-manured garden soil. To be certain that the oxygen requisite for vegetation was present in sufficient quantity, half a cubic foot of atmospheric air was drawn through the apparatus daily by means of an aspirator. But to allow of the influence of the manure being more distinctly perceived, this atmospheric air, before entering the globe, was freed from all ammonia and carbonic acid. Care was also taken to water the plants during their growth with distilled water, which was free from carbonic acid, and could be placed under the bell-glass without coming into contact with the external air. Two others, exactly like these, were placed by the side of this apparatus, which was located opposite a window situated towards the sun. One of them also contained some of the common soil which had been heated to redness in oxygen, whilst the other was furnished with the same soil which had not been heated to redness, and contained all its organic constituents. There was none of the manured garden soil in either apparatus. The barley was placed under all the three glasses in the latter days of June, from eight to ten grains beneath each. Within the first fourteen days no difference could be perceived in the development of the plants; but from this time those under the first glass differed very strikingly from the two others in which the garden mould was absent. In about three weeks the growth of the two latter was completed; the plants were between 7 and 11 inches in height: individual ones even attained a height of 17 inches, and sent forth a third or fourth leaf, but became at last white and withered; whilst, on the other hand, the plants under the first glass, which at this time were but little in advance of them, continued to grow. At the end of about eight weeks, ears began to form upon them, the number of grains in which varied from two to eight, and they had then attained a height of from 24 to 28 inches, so that they were

much bent in the bell-glass. They had also sent forth numerous shoots. They altogether acquired a much stronger appearance than those plants which had been sown in the same soil, and had grown without being covered up, whilst those sown under the bell-glass with the garden soil remained far behind them. The grains however were not developed, but were all sterile.

It is evident, from these experiments, that manure exerts an action, even when it is by no means in contact with the soil. Theodore de Saussure made a similar experiment. He allowed sweet peas to grow under a bell-glass, in the upper part of which a vessel containing manure was fixed, and also observed that the manure exerted an advantageous influence upon their growth. It might however be objected to Saussure's experiment, that he did not allow the plants to grow in earth, but in water, and only watched their development during ten days. But during this first period of development the plant still obtains enough nourishment from its own seed-grain, so that fallacy might readily ensue. In the above-mentioned experiment, however, the result is so striking as to admit of no doubt.

It might be supposed that the garden soil might have acted here merely by restoring the carbonic acid and ammonia previously removed from the air, which came into contact with the plants, and that if these had been present in the air, they would not have exerted any influence. The author regrets that the advanced autumnal season of the year did not permit the removal of this objection by comparative experiments. However, the general aspect and development of the plants under the bell-glass, where there was also garden soil, was so much stronger than in those which were developed in the same soil without being covered, that the result must be equally favourable when the air is not previously freed from these matters. But as the manure exerts so decided an action at a distance, hence by its organic constituents only, we are compelled to admit that these constituents produce the same result in the ordinarily-used manure.

The results of the preceding investigation may be summed up as follows:—

1. When mineral matters are not present, the barley only attains a height of about 5 inches, and then dies.

2. When a very small quantity of mineral matter is present, perfect development takes place.

3. If a somewhat larger quantity is present, the plant either grows in a stunted form, or is not developed at all.

4. In felspar alone barley acquires complete development and produces seeds.

5. The progress of growth varies according as the felspar is used in the state of coarse or fine powder.

6. Manure exerts its fertilizing action also at a distance. It then acts, not only by conveying certain mineral matters to the soil, but its organic constituents also contribute, and that essentially, to the promotion of vegetation.—*Monatsbericht der Akademie der Wissensch.*, zu Berlin, Feb. 1850, pp. 60–71.

Examination of the Eggs of the Carp. *By* M. Gobley.

The eggs of the carp have the greatest resemblance in their chemical composition to those of the common fowl. They appear to want the alkaline albumen which generally envelopes the yolk. The quantity of water amounts to half the weight of the eggs. The albuminous body in the eggs of carp, the *paravitelline*, has the greatest resemblance to vitelline.

The fat consists, as in the yolk of egg, of two distinct substances; the one is smeary, the other hard.

The soft fat, which forms the principal part of the eggs, is a complex compound which contains phosphorus. The author has extracted cholesterine from it, and the two substances which he also obtained from the yolk of eggs of the common fowl, and named *lecithine* and *cerebrine*.

Lecithine is the phosphorous body of hen's and carp's eggs, a neutral substance, which, on treatment with mineral acids and alkalies, constantly affords, whether the aqueous or alcoholic solution is employed, and also with the exclusion of the oxygen of the atmosphere, oleic, margaric and phosphoglyceric acids.

Cerebrine is a neutral nitrogenous and phosphorous body, which melts at an elevated temperature and swells like starch in water. The water with which the eggs have been exhausted by boiling is acid; it contains either lactic acid or some nearly-related acid. The inorganic salts contained in the eggs of the carp are identical with those found in other eggs. The yellow colouring substance of the eggs of carp appears to consist of two different bodies; one has a reddish tint, contains iron, and is probably analogous to blood-red; the other is yellow, and may be compared with the yellow colouring principle of the blood and the bile.—*Journ. de Chim. Méd.*, vi. p. 67.

On some Products of Decomposition of the Mellonide of Potassium. *By* Dr. W. Henneberg.

The mellonide of potassium can, it is true, be easily procured by the method recently described by Liebig; but the preparation of large quantities for extensive researches is accompanied with difficulties, to avoid which the author adopted the following plan.

In the first place, some tolerably pure sulphocyanide of potassium is prepared. For this purpose, 17 parts of carbonate of potash are fused with 37 parts of sulphur to a hepar, to which are added 46 parts of calcined yellow prussiate, until the mass becomes perfectly liquid and no longer exhibits the reactions of the prussiate. The fusion is effected in an iron vessel, which is well covered, at a very faint red heat, and the fire increased towards the end of the operation, in order to convert the hyposulphite of potash into sulphate. The aqueous extract of this flux generally disengages ammonia on boiling, and has sometimes a strong alkaline reaction, on which account it cannot be used directly for the preparation of sulpho-

cyanogen. The first aqueous extract, prepared by frequent boiling, is therefore neutralized when necessary with sulphuric acid, decanted from any sulphuret of iron, and evaporated to crystallization. The crystals are purified by recrystallization from alcohol.

These crystals are dissolved in water, and chlorine passed into the hot moderately concentrated solution through a tube opened out at the lower end in the form of a funnel. The current of gas must be passed in such a manner that no large masses of sulphocyanogen are formed, which would enclose chloride of potassium, as this is removed with difficulty by washing. The sulphocyanogen is reduced to a powder, and washed out with boiling water. From the wash-water a substance of a pale yellow colour is deposited on cooling, perhaps persulphocyanic acid, which is also collected and used in the same manner as the sulphocyanogen.

The calcination of the sulphocyanogen must be effected at first at the lowest possible temperature at which the sulphur is expelled. It is advisable to do this in open dishes, and to let the sulphur burn away. If the operation is conducted in retorts, sulphuret of carbon, it is true, is obtained as a collateral product; but the sulphur which distils over easily flows back into the mellone, causing this to cake together. Finally, the mass is heated in a crucible with the lid on not raising the temperature sufficiently high to cause the mass to cake together.

The colour of the mellone so obtained should be of a light yellow with a shade of gray, and not merely gray or reddish-brown. It is rubbed to powder, and strongly heated before being used.

A portion of mellone of this nature is now conveyed into from 3 to 5 parts of pure sulphocyanide of potassium, which has been previously freed from all moisture, and kept melted in a retort. The heat, moderate at the commencement, is increased as soon as the first violent disengagement of sulphurous vapours and gases has ceased, and the contents of the retort form a homogeneous mass. It is then fused at a higher temperature, avoiding the access of air as much as possible, and the operation discontinued when slender acicular needles form on cooling at those places where the fused mass has been allowed to flow down the retort in bands. If any evolution of cyanogen takes place, this indicates a decomposition of mellone, and that the maximum of temperature has been exceeded. It is difficult indeed to regulate well the temperature of a coal-fire.

The neck of the retort is now cleansed as much as possible from the brown products of distillation, the mass treated with hot water, the solution filtered, and concentrated in the water-bath after the addition of a few drops of acetic acid. In this operation, sometimes a mucilaginous substance separates, which is afterwards no longer soluble in water. To decolorize the slender acicular crystals of the mellonide of potassium thus obtained, it is most advantageous to boil the strongly diluted solution with acetic acid and purified animal charcoal; the acetic acid is each time neutralized in the filtered solution with a few drops of solution of caustic potash. To avoid the use of alcohol, which renders the decolorization very difficult,

the leys should be sufficiently concentrated before crystallization. Only in the last crystallization is alcohol added, and the crystalline mass obtained washed thoroughly with alcohol, to remove acetate of potash and sulphocyanide of potassium. In this process large quantities of mother-liquors are obtained, which it is difficult to work up.

A second method, which the author likewise employed for preparing mellonide of potassium, is that by means of the yellow prussiate, according to Gmelin's and Liebig's recent observations. The following is the plan:—1 part of calcined prussiate is fused at a gentle heat with $\frac{1}{2}$ a part of sulphur until the whole of the cyanide of potassium of the prussiate is converted into sulphocyanide of potassium; the temperature is then increased, and the whole heated until the disengagement of sulphuret of carbon ceases, and reddish cyanogen flames appear above the thickened mass. If it be then heated more strongly, and the prescribed quantity of carbonate of potash added, it may happen that not a trace of mellonide of potassium is obtained on exhaustion, but in its stead regenerated prussiate.

An addition of $\frac{1}{20}$th part of carbonate of potash relative to the amount of prussiate employed, furnishes, according to Liebig, a larger amount of product; according to the author, however, the increase is not very perceptible.

Products of Decomposition of Mellonide of Potassium: *Cyamelluric Acid, Ammelide.*—1 part of mellonide of potassium is boiled in a silver crucible with about 10 parts of solution of caustic potash of 1·2 spec. grav., and the evaporated water replaced when the mass has become thick and pasty. This operation was repeated until on sufficient concentration slender needles covered the surface, and the entire ley solidified on cooling to a paste of acicular crystals. The relative proportion of the materials above described is not of much consequence; after a single operation it will easily be seen whether a further addition of solution of potash or less dilution with water is advantageous. On the addition of the mellonide of potassium, a strong evolution of ammonia is perceptible. The crystals are washed a few times with solution of potash, and lastly with alcohol; they are then dissolved in boiling water, and the filtered liquid mixed with some alcohol, when sometimes a small quantity of a flocculent precipitate is formed, which is best separated by filtration through a funnel surrounded by hot water. On the cooling of the solution, beautiful colourless prismatic needles, frequently half an inch in length and of a vitreous lustre, are obtained. If yellowish mellonide of potassium had been employed, this product of decomposition has a yellowish appearance, which however can be removed by treatment with a little animal charcoal. These crystals are the potash salt of a tribasic acid, which the author has named *cyamelluric acid.*

Cyamelurate of Potash, $3KO, C^{12} N^7 HO^3 + 6HO$.—This salt has a strongly alkaline reaction, at first a soapy, and afterwards a bitter taste, and irritates the windpipe; in the dry state it absorbs no carbonic acid from the atmosphere. It dissolves in 7·4 parts of water at 64° F., and in 1 to 2 parts of boiling water, but not in alcohol.

The solution of the cyamelurate of potash precipitates the solutions of the earths and metallic oxides. The precipitates with sulphate of magnesia and chloride of barium are white and crystalline; the magnesia precipitate dissolves in chloride of ammonium. The copper salt is bluish-white, granular, crystalline, and appears under the microscope to consist of prisms with pyramidal terminations; it is soluble in ammonia. A yellowish, bulky, amorphous precipitate, resembling perphosphate of iron, is obtained on the addition of perfectly neutral perchloride of iron, prepared by adding a few drops of ammonia and filtering from the precipitate. The caseous, white, amorphous silver salt is somewhat sparingly soluble in dilute nitric acid. If strong nitric or muriatic acid be poured over the potash salt or these precipitates, cyameluric acid separates as a white powder. The air-dried potash salt experiences no loss in weight over sulphuric acid. The water of crystallization which it contains is entirely expelled at 212°, although it is more quickly dried at a higher temperature. It was found to contain 13·86 to 14·03 per cent. of water. This loss in weight corresponds to 6 equivs., which require 13·83 per cent. It does not lose in weight at a higher temperature. At a faint red heat the salt melts readily, with evolution of gas, when at first, but only for a short time, ammoniacal vapours are perceptible; whilst at a subsequent period, acid vapours, with the odour of cyanogen, appear. This disengagement of ammonia from the dried salt, which is only possible in the presence of hydrogen, leads the author to admit 1 equiv. hydrogen in the formula, as calculation would lead quite as well to the formula $3KO, C^{12}N^7O^8$.

The fused residue crystallizes on cooling to a radiate or acicular crystalline mass; on pouring sulphuric acid over it, it effervesces strongly, and the odour of cyanic acid is distinctly perceptible in the gas. The analysis of this potash salt furnished—

	I.	II.	III.	IV.	V.	VI.	VII.
C	..	..	..	21·62	21·56		
H	..	..	..	0·26	0·24		
N	..	..	..	..	..	29·55	29·41
KO.....	41·91	42·16	42·08				

On comparing the numbers calculated according to the two formulæ above mentioned with the mean from the preceding numbers, we obtain—

	Mean.					
C	21·59	12 = 72·0	21·41	12 = 72·0		21·47
H	0·25	1 1·0	1·29			
N	29·48	7 98·0	29·14	7	98·0	29·23
O	6·63	3 24·0	7·14	3	24·0	7·16
KO ..	42·05	3 141·3	42·02	3	141·3	42·16
	100·00	336·3	100·00		335·3	100·00

Cyamelurate of Baryta, $3BaO, C^{12}N^7HO^3 + HO$ (dried between 212° and 248°) and $3BaO, C^{12}N^7HO^3$ (dried at 482°).—Chloride

of barium was added in excess to a dilute boiling solution of the potash salt, and the liquid again heated after the precipitation. The salt so obtained consists of microscopic needles, which occupy a considerable space. It is very sparingly soluble in water. This salt contains water of crystallization, the greater portion of which escapes at 212°; the remainder appears only to be expelled at a higher temperature. The analyses of the salt, dried at different temperatures, furnished—

		Dried at 212°.	Dried at 212°.	Dried at 248°.	Dried at 482°.
C	16·82				
H	0·49				
BaO	..	52·66		53·19	54·12

If we calculate for the salt dried between 212°–248° the formula $C^{12}N^7HO^3,3BaO+HO$, we obtain 16·59 carbon, 22·59 nitrogen, 0·46 hydrogen, and 42·98 baryta. For the formula of the salt dried at 482° $=C^{12}N^7HO^3+3BaC$, we obtained 54·17 per cent. of baryta.

Cyamelurate of Silver, $3AgO, C^{12}N^7HO^3+2HO$ (dried in the water-bath).—Dried at 212°, this salt forms a white, slightly-blackened, easily-powdered mass, and still contains a quantity of water, which it retains even at 266°. The analyses of the dried salts furnished—

	I.	II.	III.	IV.	V.
C	13·07	13·17			
H	0·51	0·57			
Ag	..	..	57·88	57·67	58·03

Cyameluric Acid, $C^{12}N^7HO^3+5HO$ (and $C^{12}N^7HO^3+3HO$, when dried at 212°).—The acid is obtained as a white powder, when one of its salts is decomposed with a mineral acid. It is very sparingly soluble in cold water, requiring about 420 parts at 63°; it dissolves more readily in hot water. To purify it, it was generally boiled with water to which a few drops of muriatic acid had been added, filtered, and set aside to crystallize. In this manner, white crusts, in which some individual crystals projected, were obtained. It reddens blue litmus-paper strongly, and expels carbonic acid with the assistance of heat. It was therefore easy to prepare the salts of soda and ammonia.

When cyameluric acid is boiled with nitric acid, a crystalline product is formed, which is of the same nature as that obtained on boiling ammelide with nitric acid, and is probably cyanuric acid. Once some acicular crystals were separated from the silver salt by dilute boiling nitric acid. At a moderate red heat the dried acid turns yellow, giving off vapours of a strong odour of cyanic acid, and the glass tube in which the operation is made becomes coated with a white sublimate, which scarcely dissolves in water. With a stronger red heat, it separates in pieces from the glass tube, and evaporates, with the constant disengagement of cyanic acid; the sublimate consists most probably for the greater part of cyanuric acid.

The acid contains water of crystallization, which it parts with between 212° and 248°. The substance dried over sulphuric acid lost, upon being heated to 248°, 17·47 per cent. 5 equivs. water would amount to 16·85 per cent. The analysis of the substance, dried between 212° and 248°, furnished—

C	32·00	32·08	12 =	72	32·44
N	..	..	7	98	44·14
H	1·71	2·00	4	4	1·80
O	..	..	6	48	21·62
				222	100·00

Acid Cyamelurate of Potash, $KO, 2HO + C^{12} N^7 HO^3$ (dried at 248°).—This salt is obtained by adding acetic acid to a moderately-concentrated warm solution of the alkaline potash salt, in thin laminæ with a rainbow play of colours. From a boiling solution it separates, on slow cooling, in groups of concentrically-arranged acicular crystals. This salt is somewhat more soluble in water than the acid; it has an acid reaction, and according to its composition 2 equivs. potash of the tribasic salt are replaced by 2 equivs. water. The salt, dried over sulphuric acid, contains 4 equivs. water of crystallization, or 12·16 per cent. On calcination, the dry salt behaves like the acid, only in the present case the yellowish-brown residue fuses. This latter is soluble in water and insoluble in alcohol; the aqueous solution, on being mixed with a few drops of acetic acid, deposits a mucous mass; the liquid filtered from this precipitate possesses all the reactions of the mellonide of potassium; it is precipitated by alcohol, rendered gelatinous by muriatic acid, and forms crystals with potash which have exactly the same appearance under the microscope as the precipitate produced by potash in a solution of mellonide of potassium. The well-known cauliflower-like masses were obtained from the aqueous solution by adding some fused sulphocyanide of potassium to the yellow pulverulent residue of the calcination after the evolution of cyanic acid. A few preliminary determinations gave, for the product which had been prepared without any addition of sulphocyanide of potassium, and only recrystallized once, 33·1 dried at 356°; another, heated to a faint red, 24·4; and a third, prepared with the addition of sulphocyanide of potassium, and heated strongly over a spirit-lamp, 36·6 per cent. potash; the formula of the mellonide of potassium, $K, C^6 N^4$, requires 35·8 per cent. potash. The analysis of the acid cyamelurate of potash, dried at 248°, gave—

C	27·22	..	..	12 =	72·0	27·68
N	..	..	..	7	98·0	37·68
H	1·21	..	..	3	3·0	1·15
O	..	..	..	5	40·0	15·38
KO.....	..	18·05	17·94	1	47·1	18·11
					260·1	100·00

The compounds obtained by the author in this investigation, and described in the preceding pages, are arranged together for the sake of more easy comparison:—

Tribasic Potash Salt.

Dried in the air ..... $3KO, C^{12} N^7 HO^3 + 6$ aq.
Dried at 212° ..... $3KO, C^{12} N^7 HO^3$

Monobasic Potash Salt.

Dried over sulphuric acid .. $\left.\begin{matrix} KO \\ 2HO \end{matrix}\right\} C^{12} N^7 HO^3 + 4$ aq.
Dried at 248° ..... $\left.\begin{matrix} KO \\ 2HO \end{matrix}\right\} C^{12} N^7 HO^3$.

Acid.

Dried over sulphuric acid .. $3HO, C^{12} N^7 HO^3 + 5$ aq.
Dried at 248° ..... $3HO, C^{12} N^7 HO^3$.

Baryta Salt.

Dried at 212° ..... $3BaO, C^{12} N^7 HO^3 + HO$.
Dried at 482° ..... $3BaO, C^{12} N^7 HO^3$.

Silver Salt.

Dried at 212° ..... $3AgO, C^{12} N^7 HO^3 + 2HO$.

Ammelide is the second product of decomposition of the mellonide of potassium by treatment with potash. When the mother-liquor from which the cyamelurate of potash has separated is neutralized with acetic acid, a copious precipitate is obtained, which is washed, again dissolved with the assistance of potash or ammonia, and precipitated from this solution by acetic acid. In the dry state it forms a white powder, which dissolves in alkalies and in concentrated nitric acid. The combination with nitric acid is crystalline, and is decomposed by water. On ignition, this body at first leaves a yellowish powder, and finally disappears altogether. These properties agree with those of ammelide; moreover, the analysis of the substance, dried at 212°, furnished—

C	28·48	12 =	72	28·2
N.....	49·84	9	126	49·4
H.....	3·70	9	9	3·5
O.....	17·98	6	48	18·9
	100·00		255	100·0

*Constitution of Cyameluric Acid**.—According to Liebig the mellonide of potassium is represented by the formula $K, C^6 N^4$. The radical $C^6 N^4$ contained in this is a halogen; it behaves, according to Liebig, exactly like cyanogen. The author has therefore attempted to explain the behaviour of mellonide of potassium after the analogy of the cyanide of potassium, in the following manner:—Since cyanide of potassium, when boiled with caustic potash, is resolved, with the absorption of water, into a hydrated acid, formic acid and a basic substance, ammonia,

$$K, C^2 N + 4HO = KOC^2 HO^3 + NH^3,$$

we have for mellonide of potassium—

* See the observations of M. Gerhardt on this subject at p. 171 of the present volume.—Ed. *Chem. Gaz.*

$3C^6N^4, K+11HO+KO=C^{12}N^7$		H	O^6	3K	}	acid.
Formic acid	C^2	H	O^4	K	}	
$\frac{1}{3}$ equiv. ammelide	C^4 N^3	H^3	O^2		}	base.
2 equivs. ammonia	N^2	H^6			}	
	C^{18}	$N^{12}H^{11}$	O^{12}	K^4		

Of the products of decomposition which appear in this equation, cyameluric acid, ammonia and ammelide were obtained; the formic acid alone could not be detected. Some direct experiments which the author made for the purpose of discovering this acid proved unsuccessful. It was found impossible to separate it from the other products, although the reaction with oxide of silver and peroxide of mercury appeared to indicate its presence. Should formic acid subsequently be detected, the formula $C^{12}N^7HO^3, 3KO$ may be regarded as correct for the cyamelurate of potash.

It should be observed here, that Liebig, in his observations upon Völckel's researches on sulphocyanic acid, has already mentioned, that crude mellone, obtained by fusing sulphocyanogen, disengages ammonia by prolonged ebullition in a strong solution of caustic potash, and furnishes a readily-soluble potash salt in beautiful crystals, which have an alkaline reaction, and the concentrated solution of which, on being mixed with acetic or weak nitric acid, is converted into a sparingly-soluble acid salt, crystallizing in scales. Liebig's analyses of the silver salt gave for the dry salt, 58·4, 58·8, 58·3, 58·5 metallic silver, 48·83, 48·88, 49·06 carbonic acid, and 3·7, 4·1, 4·0 water. This would give, according to the present equivalents, 13·3 per cent. carbon and 0·44 per cent. hydrogen as the mean. The acid itself was obtained, after repeated crystallization from warm dilute nitric acid, in shining needles; it furnished 32·2, 32·3, 30·7 carbon, and 1·57, 1·86, 2·00 per cent. hydrogen.

The author finds that the description and numerical results agree in the main with cyameluric acid; and he has convinced himself that it was cyamelurate of potash by repeating the preparation of the alkaline salt from crude mellone. The acid separated by muriatic acid was however not in acicular crystals, but of the same form as the author formerly obtained.—Liebig's *Annalen*, lxxiii. p. 228.

Examination of the Berries of Myrtus communis.
By Dr. E. Riegel.

By distilling fresh ripe berries of *Myrtus communis* with water, 25 to 30 grs. of an essential oil, which entirely agreed with the oil from the leaves of this plant, were obtained. The inspissated residue of the distillation was exhausted with alcohol, which on being evaporated to an extract, parted with a greenish-brown resin to æther. On evaporating the æther, a soft resin of pungent taste was left, which is also soluble in alcohol. The portion of the alcoholic extract insoluble in æther contained tannin and sugar; the portion of the original aqueous extract insoluble in alcohol contained citric acid, malic acid, mucilage, substances resembling humic acid, potash and lime.—*Archiv der Pharm.*, lxi. p. 3.

Note on Scillitine. *By* L. F. Bley.

The author has obtained scillitine in a crystalline state, according to Lebourdais's process, by treating the aqueous extract of squills with animal charcoal. The author treated the extract of 16 oz. of squills with 12 oz. of purified animal charcoal, without any application of heat; the solution lost entirely its bitter taste. The dry charcoal was now exhausted with hot alcohol, and from this solution a small quantity of scillitine was obtained by spontaneous evaporation in long flexible needles.

The temperature at which the solution of the scillitine, from which half the alcohol had been removed by distillation, was evaporated, did not exceed 77° F. At a higher temperature it was obtained at first in oily drops, which congealed to a wax-like mass, and could not be subsequently crystallized. It must consequently have experienced some alteration, for the solution of the crystalline scillitine is neutral, and renders water turbid when added to it in drops, whilst that of the non-crystalline is acid, and does not render the water turbid.—*Archiv der Pharm.*, lxi. p. 141.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Jan. 17, 1850. (Sir Roderick I. Murchison, Vice-President, in the Chair.) The following paper was read:—

"Researches respecting the Molecular Constitution of the Volatile Organic Bases," by Dr. A. W. Hofmann.

Chemists, although all acknowledging the existence of an intimate relation between the vegetable alkaloids and ammonia, are nevertheless divided in their opinions respecting the nature of this connection, two theories having been propounded upon the subject. According to the one, that of Berzelius, the bases would have to be considered as conjugated ammonias in which ammonia still pre-exists as such; while according to Liebig's views, these substances are represented as amides, *i. e.* as ammonia in which one equivalent of hydrogen is eliminated and replaced by an equivalent of a compound radical.

The researches of the author prove that the theory of Berzelius is inadmissible, at all events for the volatile organic bases, inasmuch as in these substances ammonia ceases to exist as such. They show, moreover, that Liebig's view, although correctly expressing the constitution of by far the greater number of the volatile bases known, and presenting, when considered at the time it was first propounded, a wonderful anticipation of subsequent discovery, represents nevertheless only a special case of a much more general relation. The result at which the author has arrived is, *that ammonia is capable of losing either* 1 (*Liebig's case*) *or* 2 *or* 3 *equivs. of hydrogen which are respectively replaced by* 1, 2 *or* 3 *equivs. of the same, or various*

compound radicals, a variety of substances apparently endless being produced, in which its fundamental property (the basic character) is retained, although modified by the number of radicals introduced and their position in the scale of organic compounds.

In support of this statement, he adduces the artificial production of thirteen new organic alkaloids, formed by a method which affords the means of increasing the number of these substances to an indefinite extent. This method consists in exposing ammonia to the action of the chlorides, bromides or iodides of the alcohol radicals, which remove 1 equivalent of hydrogen of the latter, as hydrochloric, hydrobromic, &c. acid, while the remaining constituents, assuming the alcohol-radical, give rise to the formation of an organic base which unites with the hydrogen acid.

By subjecting the new base itself to a similar treatment, another equivalent of the two remaining equivalents of hydrogen may be removed, a second organic base being formed, which in its turn gives rise to a third.

The changes which the ammonia undergoes in these various processes may be represented graphically by the following simple formulæ, X, Y and Z, denoting generally compound radicals.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+XBr=\left.\begin{matrix}H\\H\\X\end{matrix}\right\}N.HBr.$$

$$\left.\begin{matrix}H\\H\\X\end{matrix}\right\}N+YBr=\left.\begin{matrix}H\\X\\Y\end{matrix}\right\}N.HBr.$$

$$\left.\begin{matrix}H\\X\\Y\end{matrix}\right\}N+ZBr=\left.\begin{matrix}X\\Y\\Z\end{matrix}\right\}N.HBr.$$

For the illustration of these general formulæ, one of the numerous sets of experiments which the author has communicated in his paper may be quoted in which X=Y=Z. Ammonia, when exposed to the action of bromide of ethyle (hydrobromic ether), is converted into hydrobromate of ethylamine, *i.e.* ammonia in which 1 equivalent of hydrogen is replaced by ethyle, a compound which was first observed by M. Wurtz under perfectly different circumstances. Ethylamine, treated again with bromide of ethyle, yields a new alkaloid diethylamine, *i.e.* ammonia in which 2 equivalents of hydrogen are replaced by ethyle, and which, under the influence of a further quantity of bromide of ethyle, lastly is transformed into triethylamine, or ammonia in which the whole of the hydrogen is replaced by ethyle. This is a most powerful alkali, whose properties resemble those of caustic potassa.

Jan. 24, 1850. (Richard Owen, Esq., Vice-President, in the Chair.) The following paper was read:—

"Observations on the Freezing of the Albumen of Eggs," by James Paget, Esq., Professor of Anatomy and Surgery to the Royal College of Surgeons.

The object of this paper is to illustrate a peculiar property of the albumen of the eggs of birds, a property which seems to have its purpose in preserving them from the injurious effects of very low temperatures.

Mr. Hunter observed that a fresh egg will resist freezing longer than one which has been previously frozen and thawed; and he referred this fact to the 'vital power' of the egg in the first case, and the destruction of that power by freezing in the second. The author's experiments confirm those of Mr. Hunter, and prove, also, that when fresh eggs are exposed to very low temperatures, and also in the case of eggs which are decayed, or putrid, or the contents of which have been much altered by mechanical force or by electricity, a shorter time is sufficient for the freezing of such eggs, than is necessary for the freezing of those which are uninjured.

An examination of the rates at which heat was lost by the several eggs, exposed to temperatures varying from zero to 10° Fahr., showed that fresh eggs, though they resist freezing longer than any others, yet lose heat more quickly; and that their resistance to freezing is due to the peculiar property of their albumen, the temperature of which may be reduced to 16° Fahr., or much lower without freezing, although its proper freezing-point is at or just below 32°. Other than fresh eggs lose heat comparatively slowly, but freeze as soon as their temperature is reduced to 32°; fresh eggs lose heat more quickly, but may be reduced to 16° or lower; then, at the instant of beginning to freeze, their temperature rises to 32°.

That this peculiarity of fresh eggs is not due to vital properties, is proved by experiments which show that certain injuries, such as mechanical violence, addition of water, and others, which spoil their powers of resisting freezing, do not prevent eggs from being developed in incubation. By the same and other experiments, which are related, it is made probable that the peculiarity depends on the mechanical properties of the albumen; for, whatever makes the albumen more liquid than it is naturally in the fresh egg, destroys the power of resisting freezing.

The author could find no other substance possessing this property; and in evidence of its adaptation to the purpose of preserving eggs from the loss of their capacity of developement, which they would suffer in being frozen, he relates experiments in which eggs were kept for a considerable time at temperatures ranging from zero to 10° Fahr., yet were afterwards developed in incubation. By the same series of experiments it was shown, that, although freezing renders the effectual developement of the germ impossible, yet the intensest cold, if freezing does not take place, has no similar result.

March 14, 1850. (George Rennie, Esq., Vice-President and Treasurer, in the Chair.) The following paper was read:—

"On so-called Chylous Urine," by H. Bence Jones, M.D., A.M., F.R.S. &c.

The definition given of chylous urine is, that it is urine which is white from the suspension of fatty matter in it. An opportunity of

observing a case of this disease having occurred to the author, he was led to make the experiments described in this paper. A harness-maker, age 32, half-caste, who had lived in London for twelve years, had been passing such water for nine months. On examination of the water made at 2 P.M. it solidified, looking like blanc-mange in ten minutes. It was very feebly acid, contained fibrine, albumen, blood-globules and fat; specific gravity=1015. 1000 grs. of this urine gave—

44·42 grs. total solid residue.
8·01 grs. total ash.
14·03 grs. albumen.
8·37 grs. fat.
13·26 grs. urea and extractive matter.
·75 gr. loss.
955·58 grs. water.

In order to watch the variations produced by food and exercise in the appearance of the urine, every time the urine was made, for five days and nights it was passed into bottles marked with the hour. From these observations, and more particularly from the third, fourth, and sixth days, it was evident that the fibrine and albumen appear in the urine when no fat is there, and that the albuminous urine occurs before food has been taken, and disappears during the night with perfect rest. Thus the fourth day, at $7^h\ 15^m$ A.M., on first getting up the urine contained the slightest trace of albumen. The specific gravity=1027; the precipitate by alcohol=0·8 gr. per 1000 grs. urine.

At $9^h\ 50^m$ A.M., just *before* breakfast, the urine formed a solid coagulum free from fatty matter, but contained a visible deposit of blood. Specific gravity=1015·6; the precipitate by alcohol=14·1 grs. per 1000 grs. of urine.

At 11 A.M., the urine was chylous or white from fatty matter.

Further experiments on the influence of rest and motion in lessening or increasing the albumen in the urine previous to food are then given.

On five different mornings, by rising early or late, and by collecting the precipitate from the urine by alcohol, the influence of rest and motion was determined. The author states that he could fix beforehand whether the urine should be albuminous or not, by directing the patient to get up, or to lie still.

The patient was bled and the serum was opalescent, but did not clear with æther: the blood contained no excess of fat. 1000 parts of blood gave—

2·63 grs. fibrine.
159·3 grs. blood-globules.
78·1 grs. solids of serum.
240·03 grs. total residue.
759·97 grs. water.

The urine made the same day was examined at different hours; that made immediately before the bleeding was quite white, and that

made an hour and a half afterwards was very milky also. Specific gravity=1018. 1000 grs. of urine gave—

56·87 grs. total residue.
10·80 grs. total ash.
13·95 grs. albumen.
7·46 grs. fat.
24·06 grs. urea, &c.
·60 gr. loss.
943·13 grs. water.

The conclusions from these experiments are,—

1. That so-called chylous urine, besides fat, may contain albumen, fibrine, and healthy blood-globules.

2. That, although the fat passes off in the urine after food is taken, yet the albumen, fibrine and blood-globules are thrown out before any food has been taken. During perfect rest the albumen ceases to be excreted; and it does not appear in quantity in the urine even after food is taken, provided there is perfect rest. A short time after rising early the urine may coagulate spontaneously, although no fat is present; and this may happen previous to food, when the urine is free from fat.

3. Though the urine made just before and a short time after bleeding was as milky as it usually was at that hour of the day, yet the serum of the blood was not milky: it did not contain a larger quantity of fat than healthy blood does.

The general results are,—

1. That the most important changes in the urine in this disease take place independently of the influence of digestion.

2. That the urine in one respect only resembles chyle, and that is in containing, after digestion, a large quantity of fat in a very fine state of division. The supposition that the disease consists in an accumulation of fat in the blood, which is thrown out by the kidneys, carrying with it albumen, fibrine, blood-globules and salts, is altogether disproved, both by actual analyses of the blood, and by the frequent occurrence of a jelly-like coagulum in the urine when no white fatty matter can be seen to be present.

3. The disease consists in some change in the kidney by which fibrine, albumen, blood-globules and salts are allowed to pass out, whenever the circulation through the kidney is increased; and if at the same time fat is present in the blood, it escapes also into the urine. That this change of structure is not visible to the naked eye on post-mortem examination, Dr. Prout long since demonstrated; and in a case of this disease which was in St. George's Hospital, and was examined at Plymouth, no disease of the kidney was observed. From the total absence of fibrinous casts of the tubes from the urine, it is not improbable that by the microscope a difference may be detected in the structure of the mammary processes, rather than in that of the cortical part of the kidneys.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Borax. By Prof. E. Schweitzer.

The influence which external conditions exert upon the affinity of bodies occurs in a very remarkable degree in boracic acid; whilst boracic acid at the ordinary temperature has nearly the least affinity of all acids towards bases, it is capable at an elevated temperature of expelling the strongest acids from their compounds. In the aqueous solution of the borates, boracic acid exhibits a far smaller affinity than in the dry salts; and several known facts tend to show, that on diluting the solution of borates, the affinity of the boracic acid decreases in proportion; whilst, on the contrary, on heating such a solution, the affinity is again increased. When boracic acid is in the presence of any other acid, the limits within which the various expressions of the affinity of the boracic acid take place are the further removed the greater the difference in strength of the two acids, and *vice versâ*.

Starting from these views, the author has examined the deportment of those acids towards borax, which in respect to their affinity come very near to boracic acid.

Carbonic Acid and Borax.—When borax is fused with carbonate of soda, the carbonic acid, as is well known, is expelled and neutral borate of soda formed; this decomposition also takes place when a solution of borax is boiled with carbonate of soda. When, on the other hand, neutral borate of soda is exposed to the atmosphere in crystals or in the state of solution, it is gradually converted, by the absorption of carbonic acid, into borax and neutral carbonate of soda. On passing a current of carbonic acid through a cold saturated solution of borax, a considerable quantity was found to be absorbed, as a lively effervescence ensued upon the subsequent addition of a stronger acid. A solution of borax, which has been treated in this manner with carbonic acid, has a faint acid reaction; if it be evaporated, it disengages, at a certain degree of concentration, carbonic acid in considerable quantity, and pure borax is left behind.

To determine the quantity of carbonic acid which a solution of borax is capable of fixing, 4·000 grms. of borax ($NaO, 2BoO^3 + 10HO$) were dissolved in the requisite amount of cold water, and a

slow current of carbonic acid passed through the solution for several hours. After the carbonic acid held only in mechanical solution, had been removed by shaking the liquid and exposing it to the air, the combined carbonic acid was estimated according to the method of Will and Fresenius. 0·435 grm. of carbonic acid was obtained; consequently 100 parts of crystallized borax absorb 10·90 parts of carbonic acid, which quantity exactly suffices to convert the soda into neutral carbonate of soda. According to theory, 100 parts of borax contain 16·35 parts soda, which require 11·40 carbonic acid to form NaO, CO^2.

When a solution of borax, completely saturated with carbonic acid, is mixed with an equal volume of alcohol, no borax separates even after a long interval; when, on the contrary, a very dilute solution of pure borax is mixed with alcohol, the borax is almost immediately and wholly precipitated in the crystalline state. It is evident therefore that no borax is any longer contained in the solution saturated with carbonic acid.

Sulphuretted Hydrogen and Borax.—Sulphuretted hydrogen gas is absorbed in large quantity by an aqueous solution of borax. On mixing the saturated solution with muriatic acid, a violent effervescence results from the gas, which again makes its escape. If the liquid be concentrated by evaporation, the whole of the sulphuretted hydrogen is likewise gradually given off, and on cooling, pure borax crystallizes out. If it be exposed for some length of time to the air, there is no longer any disengagement of sulphuretted hydrogen on the addition of muriatic acid; whilst on boiling the liquid with this acid, a copious evolution of sulphurous acid takes place, and sulphur separates. There was consequently hyposulphite of soda present, which must have been formed by the oxidation of sulphuret of sodium.

A slow current of sulphuretted hydrogen was passed for a long time into a cold solution of borax, and the latter subsequently mixed with twice its volume of alcohol. No separation of borax took place; only after a long interval a few minute crystals of borax formed at the bottom of the vessel, a proof that the decomposition by sulphuretted hydrogen had not been quite complete. The alcoholic solution was now mixed with æther until two strata formed; the lower yellowish one was a concentrated solution of *sulphuret of sodium* in water; the upper layer furnished, on evaporation, scaly crystals, which on accurate examination proved to be *pure boracic acid.*

These experiments demonstrate, that, in the action of sulphuretted hydrogen on borax in the dissolved state, sulphuret of sodium is formed and boracic acid eliminated. The borax is consequently decomposed by sulphuretted hydrogen entirely into acid and base, so small is the affinity of the 2 atoms of boracic acid to the 1 atom of soda in the cold solution of the borax. On heating and concentrating the solution, the affinity of the boracic acid is so much increased, that it is capable of again decomposing the sulphuret of sodium.

Carbonic acid also decomposes an aqueous solution of borax. It

could not be ascertained by experiment whether in this case boracic acid is separated as such. The decomposition may therefore be imagined to be such that the carbonic acid deprives the borax of half the soda, and forms bicarbonate of soda, whilst the quadriborate of soda discovered by Bolley is formed—

$$2(NaO, 2BoO^3) + 2CO^2 = NaO, 4BoO^3 + NaO, 2CO^2.$$

It is however far more probable that the action of the carbonic acid is identical with that of the sulphuretted hydrogen, since the affinity of carbonic acid is in general somewhat stronger than that of sulphuretted hydrogen, and the carbonic acid would therefore be more able to deprive the boracic acid of the whole of the soda than the sulphuretted hydrogen. The circumstance that alcohol produces no precipitate in a solution of borax decomposed by carbonic acid, and which would certainly happen if quadriborate of soda were present, speaks in favour of this view.

According to this, borax is decomposed by carbonic acid into neutral carbonate of soda and boracic acid—

$$NaO, 2BoO^3 + CO^2 = NaO, CO^2 + 2BoO^3.$$

The reason why no bicarbonate of soda is formed is probably owing to the presence of the free boracic acid, which prevents any further absorption of carbonic acid.

Barreswill has hinted that borax experiences a decomposition on solution in much water, similar to that of the salts of bismuth and the soaps under the same circumstances. If crystallized borax is regarded as a neutral salt, it ought, according to Barreswill, to be considered, when in a very dilute solution, as a neutral compound mixed with a basic salt and free acid. He based this view upon the fact, that chlorine is absorbed by a dilute solution of borax, and precisely so as if the base were contained in it in a perfectly free state; the same applies to iodine and bromine. Sulphur dissolves in borax, as in free alkalies, and expels the boracic acid. Sulphuret of sodium and hyposulphite of soda are formed. The more dilute the solution of borax, the more sulphur dissolves in it.

That water is capable of diminishing, nay even of suspending, the affinity of boracic acid towards the bases, is proved most evidently by the observation of Rose, that on mixing a very dilute solution of borax with nitrate of silver, no borate of silver, but pure oxide of silver is precipitated. The view that borax experiences decomposition on solution in water is therefore highly probable; regarding borax, as is generally admitted, as a biborate of soda, the decomposition would consist in the water depriving the compound of half the boracic acid, neutral borate of soda being formed. This neutral borate is decomposable by the weakest acids, and the more easily the diluter the solution.

The experiments above described, on the action of carbonic acid and of sulphuretted hydrogen upon dissolved borax, go to show that in a cold saturated solution the borax is not merely partially decomposed, as assumed by Barreswill, but entirely into boracic acid and

neutral borate of soda, perfect decomposition being produced in such solution by the above acids.

Silicic Acid, in its soluble modification, has no decomposing action upon a solution of borax. The author mixed some pure gelatinous silica, obtained by decomposing fluoride of silicon by water with a very dilute solution of borax, and set the whole aside for a considerable length of time, frequently shaking it. The filtered liquid contained but a trace of silicic acid, and unaltered borax was separated by alcohol. Silicic acid stands therefore, as regards its affinity towards bases, lower in the scale than boracic acid, whilst the latter is surpassed by carbonic acid and sulphuretted hydrogen.

Analysis of Borax.—On the occasion of examining the compound treated of in the following section, the author discovered a very simple and accurate method of determining the amount of the alkalies in boracic compounds, and which is immediately applicable to the analysis of borax, and may also be advantageously employed in many other cases. This method is founded on the circumstance, that on mixing a solution of borax with muriatic acid and evaporating to dryness, the whole of the soda is contained in the residue in the state of chloride of sodium, the boracic acid exerting under these circumstances no reciprocal affinity.

The estimation of the soda in borax is made therefore as follows:—The weighed amount of borax is dissolved in water, an excess of muriatic acid added to it, and the solution evaporated on the water-bath. Towards the end of the operation, a few drops more muriatic acid are added. The perfectly dry mass is then redissolved in water, a little nitric acid mixed with the solution, and the chlorine precipitated by nitrate of silver; from the amount of chloride of silver that of the chlorine is deduced, and from that the quantity of soda.

The following are the results of an analysis of borax, in which this method of estimating the soda was employed. The borax was perfectly purified by repeated crystallization. 2·00 grms. borax lost on ignition 0·941 grm. water. 2·00 grm. borax furnished 1·494 grm. chloride of silver =0·3258 soda. 100 parts of borax contained therefore, according to this analysis—

		Calculated.	Analysis by Berzelius.
Soda	16·29	16·35	16·31
Water.....	47·05	47·17	47·10
Borax.....	36·66	36·48	36·59

This method furnishes therefore as accurate a result as that of Berzelius, in which the borax is decomposed by hydrofluoric acid.

Borax and Arsenious Acid.—A saturated solution of borax readily dissolves a large amount of arsenious acid without any elimination of boracic acid; a compound of boracic acid, arsenious acid and soda is formed, which is distinguished from the substances from which it has originated by its great solubility in water.

The following was the method employed for obtaining this compound in the pure state:—A cold saturated solution of borax was heated for a long time with an excess of finely-powdered arsenious

acid upon the water-bath. The liquid was then filtered from the undissolved arsenious acid, concentrated on the water-bath, and set aside, when some crystals of unaltered borax separated. It was then further evaporated to the thickness of a syrup, and the syrup mixed with a little water, when a large quantity more borax separated. The liquid portion was passed through a strainer, again concentrated, and left in the cold for several days. Some brownish flakes now separated, but no more crystals of borax. The liquid separated from the flocculent precipitate was now evaporated to dryness; the residue remained for a long time soft and tenacious, but after several days' heating it became perfectly solid and brittle, forming a transparent gummy mass of a faint yellowish colour. To obtain it perfectly pure, it was dissolved in the least possible quantity of water, the solution decanted from a small quantity of arsenious acid which had separated, and evaporated under the air-pump. During the evaporation the syrup remained perfectly clear. The solid mass was left for several weeks under the air-pump, to obtain it perfectly dry.

The new compound is exceedingly soluble in water. In a very small quantity of water it dissolves however only slowly to a syrup. In alcohol it is nearly insoluble. The aqueous solution has an alkaline reaction, and becomes turbid after a time by exposure to the air, undoubtedly owing to some arsenious acid being eliminated by the carbonic acid of the atmosphere. When heated in a glass tube, it puffs up considerably, disengaging aqueous vapours; arsenious acid sublimes, and metallic arsenic is eliminated.

It does not separate from the aqueous solution in a crystalline state, even on very slow spontaneous evaporation. Only once a few white spherical bodies were formed in such a solution. A syrupy solution of the substance congeals in snow to a white radiately-crystalline mass, which immediately becomes liquid on being removed from the snow.

The analysis of this compound presented considerable difficulty. It was impossible to determine the water directly in any manner, as the compound is decomposed whether heated alone or with bases. By applying the method above described, the author succeeded in determining the amount of boracic acid approximatively; the quantity of the water was deduced from the loss.

2·00 grms. of the compound were dissolved in water, the solution acidified with muriatic acid, and the arsenious acid precipitated by sulphuretted hydrogen in the form of sulphuret, from which the amount of the former was determined in the usual manner. 1·11 grm. of arsenious acid was obtained. The acid liquid filtered from the sulphuret of arsenic was now evaporated to dryness in the water-bath, the dry residue dissolved in water, the solution mixed with a little nitric acid, and the chlorine precipitated by nitrate of silver. From the quantity of the chloride of silver, the quantity of soda could be calculated; 0·966 chloride of silver was obtained =0·210 soda.

A second analysis, made in the same manner, gave for 2 grammes

of the compound 1·368 sulphuret of arsenic =1·102 arsenious acid. The solution, freed from the arsenious acid, was now supersaturated with ammonia and evaporated to dryness, adding from time to time a little concentrated ammonia, in order to prevent the volatilization of the boracic acid with the aqueous vapours, so that the whole amount of it was contained in the residue. This, which consisted of chloride of sodium, chloride of ammonium and borate of ammonia, was heated to redness and weighed. On calcination, the chloride of ammonium and the ammonia of the borate of ammonia were expelled. The liberated boracic acid may possibly have decomposed a portion of the chloride of sodium, so that the calcined residue consisted of chloride of sodium, boracic acid and borate of soda.

Its weight gave consequently the whole amount of the boracic acid +that of the soda, the latter partly as such and in part as chloride of sodium. It amounted to 0·773 grm. The residue was then dissolved in water, a few drops of nitric acid added to the solution, and the chlorine precipitated by nitrate of silver. 0·790 grm. chloride of silver was obtained, which corresponds to 0·324 chloride of sodium. If we now deduct the chloride of sodium from the total, we obtain the weight of the boracic acid and of the soda combined with it. With these data we arrive at the following composition:—

Arsenious acid	55·55	5	= 55·79
Soda	10·50	3	10·55
Boracic acid	20·55	6	23·53
Water.....	13·40	10	10·13

The loss in boracic acid is undoubtedly owing to the circumstance, that in the decomposition of the borate of ammonia some boracic acid must have been volatilized with the water. The compound contains the constituents of 3 atoms of borax and 5 atoms of arsenious acid. As, on heating the compound, on the one hand metallic arsenic is eliminated with the formation of arseniate of soda, and on the other hand arsenious acid is sublimed, it must be assumed that a portion of the arsenious acid is combined with soda, whilst another portion is present in a more loose state of combination, undoubtedly with boracic acid. On the assumption that the whole of the soda is combined with arsenious acid, forming acid arsenite of soda, the formula $3(NaO, AsO^3)+2(3BoO^3, AsO^3)+10HO$ might be advanced. But it is not probable that (even though the arsenious acid completely decomposes the borax in the aqueous solution) the boracic acid should not, on subsequent concentration, again appropriate a portion of the soda. The proximate constituents of the compound are therefore without doubt *arsenite of soda, borate of soda* and a compound of *arsenious acid* with *boracic acid*; but then there are various modes of viewing the constitution of the compound, among which the author gives a preference to the following:—

$$NaO, AsO^3+2(NaO, 2BoO^3)+2(BoO^3, 2AsO^3)+10HO.$$

Organic Acids and Borax.—Benzoic acid is dissolved in considerable quantity, even in the cold, by a solution of borax. A cold

saturated solution of borax was digested with an excess of benzoic acid at a gentle heat, and the filtered liquid then concentrated on the water-bath. The solution was now set aside to cool; after twelve hours no crystals had separated, but on accidentally shaking the liquid, a quantity of crystalline scales formed in it, which proved to be pure *boracic acid.* The separated solution gave, on further slow evaporation, a considerable quantity of columnar, and then acicular crystals of *benzoic acid.* The former were of considerable size, possessed great lustre, and were perfectly transparent, but immediately became white and opake on contact with pure water. On recrystallization, it was obtained in the form in which benzoic acid usually crystallizes from an aqueous solution. The thick liquid separated from the benzoic acid furnished no more crystals on further evaporation, but left a white silky mass, which dissolved very readily in water, but did not separate in a crystalline state on very slow evaporation of its solution, but only in aggregated spherical masses.

This compound consists of *soda, boracic acid, benzoic acid* and *water.* It dissolves very readily in alcohol, by which it is distinguished especially from the benzoate of soda. Its aqueous solution possesses a pungent taste, with a sweetish after-taste.

The action of benzoic acid upon borax differs therefore from that of the arsenious acid insofar that in the first instance a portion of the boracic acid of the borax is actually eliminated. Further, on concentrating the liquid, the free or loosely-combined boracic acid exerts its affinity, and expels a part of the benzoic acid; but there finally remains a peculiar compound, which consists of benzoic acid and the constituents of the borax. It is probable that the benzoic acid decomposes the borax entirely, and forms benzoate of soda and free boracic acid, but that a portion of the latter converts the benzoate of soda into the new compound upon evaporation, with elimination of benzoic acid.

Tannic Acid and Gallic Acid behaved like arsenious acid towards borax. Combinations of tannic and gallic acids, with the constituents of the borax, are formed without any elimination of boracic acid; they are also very soluble in water; the gallic acid compound forms, in the dry state, a gummy mass, that of the tannic acid a yellowish powder. The latter no longer possesses the astringent taste of the tannic acid. When an aqueous solution is mixed with an acid, the whole congeals to a gelatinous mass, undoubtedly owing to the separation of the compound of tannic and boracic acid observed by Berzelius.

Margaric, Stearic and Oleic Acids dissolve in considerable quantity in a solution of borax. The clear solution, saturated with stearic acid with the assistance of heat, entirely solidifies on cooling to a gelatine. *Colophony* is likewise readily soluble in a solution of borax.

Amorphous Hydrated Borax.—It is well known that borax is obtained in two different crystalline forms, combined with different amounts of water according to the temperature at which it crystal-

lizes. Below 133° it crystallizes in oblique rhombic prisms, with 10 atoms of water of crystallization; this is the ordinary borax, $NaO, 2BoO^3 + 10HO$. Above 133° it separates in octahedra, with 5 atoms of water of crystallization, $NaO, 2BoO^3 + 5HO$.

If a solution of borax be evaporated on the water-bath at 212°, the borax is left as a perfectly amorphous, transparent, brittle mass. If, during the evaporation, the temperature sink below 194°, the borax is obtained in the crystalline state. To determine the amount of water in the amorphous compound, it was heated on the water-bath at 212° till it lost no more in weight, and a weighed quantity then calcined. It contained 26·60 per cent. water, which forms exactly 4 atoms of water to 1 atom of anhydrous borax:—

	Found.	Calculated.
$NaO, 2BoO^3$	73·40	100·8 = 73·68
$4HO$	26·60	36·0 26·32

Mitth. der Naturforsch. Gesellsch. zu Zürich, 1850, p. 1.

Observations on the Essential Oil of Bitter Almonds.
By C. G. Mitscherlich.

The author has studied the action of the essential oil of bitter almonds upon rabbits. The most accurate experiments which have hitherto been made known upon this subject are those of Wöhler and Frerichs*, who showed that 2 grms. of the oil, administered to a small dog, produced illness, without however causing death. The urine of the dog contained hippuric acid. Former statements respecting the violent poisonous properties of this oil were shown to be owing to the difficulty of obtaining the oil perfectly pure from prussic acid.

The author employed an oil which was freed from prussic acid by agitation with lime, a protosalt of iron, and subsequent distillation. The result of Mitscherlich's investigations is as follows:—

In quantities of 2 and 1 drms. of the oil, injected into the stomach of the animals by means of an elastic tube, it acted as a strong poison, not so violent as the essential oil of mustard, but more so than the essential oils of Junip. Sabina, Sem. Carui, Cort. Cinnamomi, Nux moschata, Sem. fœniculi, turpentine, lemon and balsam copaivæ. It is absorbed in the stomach, and again partially excreted by the kidneys and lungs. When given in small doses, it is, as stated by Wöhler and Frerichs, oxidized in the body, and converted into hippuric acid; but in larger doses the oxidation is not perfect, a portion of the oil passes unaltered into the urine, and may be detected in it as well as in the expired air. The principal symptoms evident when it leads to death are quick destruction of voluntary motion and sensibility, during which the breathing and pulsation of the heart, both of which are hastened by the poison, still continue.

It causes a similar alteration in structure in the intestinal canal as

* Chem. Gaz., vol. vi. p. 230.

the oils of caraway, lemon, cinnamon, turpentine, fennel, copaiva balsam, &c.

Oil of bitter almonds which has not been freed from prussic acid acts as a poison in small doses from the prussic acid present only. Administered in quantities of 1 scruple to rabbits, it did not produce any violent symptoms of disease. It has the destructive action in common with many other essential oils, which likewise are not poisonous in very small quantities.—Buch. *Rep.*, iv. p. 267.

On Guaicuru Root. By M. Lenoble.

In the Republic of Uruguay (Monte Video) there grows a root, called by the Indians Guaicuru, which has great resemblance to *Polygonum bistorta*; externally its colour is reddish; its taste is astringent. The natives of the district hold it in high estimation. It is used,—1st, in syphilitic diseases; 2nd, in hæmorrhage; 3rd, in hæmorrhoids.

The author exhausted the root in a displacement apparatus. Ordinary sulphuric æther is coloured greenish-yellow by it, acquires an astringent taste, and reddens blue litmus-paper. On evaporation to dryness, this extract left a chestnut-brown residue, nearly the whole of which was soluble in water, and was precipitated by gelatine in white flakes; a solution of iron gave with it a bluish-black precipitate. That which was left undissolved by the water appeared to be of a resinous nature.

Distilled water extracted a reddish colouring substance from the root, which had an astringent taste, and reddened blue litmus-paper. Gelatine and a solution of iron behaved as above towards this solution. When mixed with hydrate of lime, the solution disengaged ammonia.

On dry distillation in a glass tube, the root gave off ammoniacal vapours. The substances detected in the root are limited therefore to,—1st, tannic acid; 2nd, resin; 3rd, red colouring principle, soluble in water and in alcohol; and 4th, ammoniacal salts.—*Journ. de Pharm.*, xvii. p. 199.

On Aridium, a probably new Metal. By M. Ullgren.

Prof. Wallmark has recently communicated to the Academy of Sciences of Stockholm a paper by M. Ullgren, in which he gives an account of a probably new metal, occurring in the chrome iron of Röros, and some other iron ores. The metal exhibits in its oxides great resemblance to iron, on which account it has been named aridium.

The author found, in some experiments made with a view to detect the presence of phosphorus in the bar iron of Oernstolsos iron ores, that the solution of iron obtained behaved in several respects differently towards reagents from one of iron only. The author subsequently found, in an examination of the chrome-iron of Röros,

that the peroxide of iron separated from it behaved like that in the first-mentioned solution.

The chrome-ore, reduced to powder, was digested with muriatic acid, the greenish-yellow solution evaporated to dryness, the silica separated in the usual manner, and sulphuretted hydrogen passed through the solution to perfect saturation. A very small quantity of a grayish-yellow precipitate, which consisted principally of sulphur, was thus obtained. In order however to be certain of separating every metallic sulphuret insoluble in an acid liquid, the solution was neutralized with caustic potash, mixed with sulphuret of potassium, and now so much muriatic acid added to it that the black precipitate produced was again dissolved. An inconsiderable pale yellow residue was left, and the solution was of a beautiful green colour, proceeding mostly from the oxide of chromium which the muriatic acid had extracted from the chrome-iron ore. The solution was now heated with chlorate of potash and excess of muriatic acid, and then precipitated at a boiling temperature with potash. The alkaline liquid was yellow, and contained chromic acid and alumina. The precipitate was brownish-yellow; it was dried, rubbed to powder, and fused in a platinum crucible with a readily-fusible flux and chlorate of potash. On exhausting the fused mass with water, only chromic acid and some alumina could be detected in the yellow solution. The occurrence of the latter led the author to dissolve the liver-coloured residue again in muriatic acid, and precipitate afresh with caustic potash and wash with boiling water. The washed brown residue was now dissolved in muriatic acid, the solution mixed with a sufficient quantity of acetate of soda, diluted and boiled. A light reddish-brown, pulverulent, and not a bulky, flocculent or brown precipitate, like peroxide of iron, was obtained; manganese, lime, magnesia and a trace of zinc remained in solution. The precipitate was now dissolved in muriatic acid, and the solution saturated with caustic ammonia. The precipitate produced formed blackish-brown lumps, which when dry did not present a glassy, but an earthy fracture. This precipitate was now treated in the following manner:—A portion was dissolved in muriatic acid, and the muriatic acid expelled by ebullition with an accurately-measured quantity of sulphuric acid, and evaporated to dryness. The residue formed a whitish-yellow mass, interspersed with crystalline scales, and which was still moist with the excess of sulphuric acid. It was dissolved in alcohol of 0·86 spec. grav., and 6 times the bulk of æther added to it. The liquid instantly became milky, and in the course of an hour the small eliminated drops had collected together to a thick syrup at the bottom of the vessel. The clear decanted liquid was again rendered turbid by a further addition of æther. After expelling the æther and alcohol, a thick liquid was left, in which some blackish-brown flakes floated, which however did not consist of an organic substance produced by the action of the sulphuric acid upon the alcohol, as was at first suspected; for when burnt, they became grayish-white, and gave with borax and microcosmic salt colourless beads, and a yellowish-gray opalescent bead

with soda upon platinum wire. The liquid separated from these brown flakes deposited, on slow evaporation, after forty-eight hours, some small crystals cohering to verrucous masses, which were rinsed with alcohol, in which they are very sparingly soluble. These crystals are the sulphate of the peroxide of aridium.

Another portion of the same peroxide of iron, which had been used in the preceding examination, was now heated to redness in a current of hydrogen until no more water was given off; the residue was treated with dilute nitric acid, in which a portion dissolved with disengagement of nitric oxide, which however soon ceased, when a black, somewhat brownish powder was left. This powder was magnetic, but the solution behaved like one of pure peroxide of iron. The powder was certainly an oxide, as it dissolved in muriatic acid without disengagement of gas. It was now packed into a charcoal crucible, covered with some cyanide of potassium, and heated in the forge-furnace. The powder had caked together by this treatment, had acquired an iron-gray colour, and here and there some small fused gray metallic granules occurred. Dilute nitric acid now dissolved a small portion with evolution of gas, but it soon ceased, and left a residue which dissolved no further in it. What the nitric acid had dissolved, in this and the preceding case, after the treatment with hydrogen, was peroxide of iron. The insoluble portion was now no longer magnetic, and dissolved in concentrated muriatic acid without disengagement of gas. This residue is therefore, like the protoxide of uranium, a lower oxide of aridium, which cannot be further reduced in the charcoal crucible. The following is the behaviour, as far as it has yet been ascertained, of the oxide in question, which justifies its being regarded as the oxide of a new metal:—

1. It dissolves in muriatic acid without disengagement of chlorine, and furnishes, on evaporation at a gentle heat, a lemon-yellow deliquescent residue, which cannot be made to crystallize. It differs in this respect from the oxide of iron and the oxide of cerium.

2. It gives a compound with sulphuric acid, which yields a colourless solution with water, differing from the persulphate of iron, at least in the presence of free acid. On ignition, this sulphate left a reddish-brown powder, which appeared under the microscope as small indistinct transparent crystals of a beautiful red colour.

3. When sulphuretted hydrogen was passed through the solution of this metal, the oxide was reduced to protoxide. After expelling the excess of sulphuretted hydrogen, it was precipitated of a grayish-white colour by ammonia; but this precipitate immediately passed into light brown, and not, as in the case of the protoxide of iron, first through green into brown.

4. The fresh solution of the protoxide is precipitated by the ferrocyanide of potassium of a pale whitish-green colour, which gradually changes into dark green, and afterwards becomes bluish. If an excess of ammonia is poured over it, it becomes of a beautiful blue; but this colour gradually disappears, and it finally turns grayish-blue.

5. A solution of the protoxide of aridium is not precipitated by an infusion of galls. Acetate of soda gives a pale red precipitate.

6. A solution of the peroxide of aridium does not strike a black, but a dark indigo-blue colour with an infusion of galls, and furnishes upon the addition of acetate of soda a brownish-violet precipitate. Neither iron nor cerium behaves in this manner.

7. A solution of the peroxide of aridium gives a dark blue precipitate with ferrocyanide of potassium; but an excess of the precipitant changes the colour into a dirty bluish-green. Cerium gives a white precipitate.

8. A solution of oxide of aridium is coloured bluish-green by the ferridcyanide of potassium, and deposits in the course of an hour in the dark a precipitate of the same colour. A solution of peroxide of iron is coloured brown; cerium is not precipitated.

9. A solution of the peroxide of aridium is not precipitated, like a solution of iron, of a deep blood-red by acetate of soda, but dark yellowish-brown.

10. A solution of the peroxide of aridium strikes a deep red colour with sulphocyanide of potassium, like a solution of the peroxide of iron; but in the case of iron, the colour disappears with an excess of acid, whilst with the peroxide of aridium it remains even with a large excess of acid.

11. A solution of the peroxide of aridium gives a light brownish-yellow precipitate with carbonate of soda and a yellow solution; peroxide of iron, on the contrary, gives a brownish-red precipitate, which also dissolves with a red colour.

12. The alkaline sulphurets produce a blackish-green precipitate, and the solution continues long green. The precipitate dissolves readily in dilute nitric acid.

13. Solutions of the oxide of aridium furnish with caustic alkalies precipitates like those produced in solutions of the peroxide of iron, only they are somewhat yellower and more earthy when dried. After ignition, the powder is grayish-brown, and not so red as the peroxide of iron.

14. *Before the blowpipe oxide of aridium* gives with borax, on platinum wire in the outer flame, a yellow bead, which becomes colourless on cooling with small quantities. In larger quantities, the bead is of a brownish-red; on cooling, yellow and opalescent, but not as with cerium. In the inner flame, the bead is coloured of a light green by small quantities, and becomes colourless on cooling; with a larger quantity, the bead is of a beautiful green while hot; the purity of the colour decreased as it cooled.

With microcosmic salt and strong saturation, the bead while hot was dark red in the outer flame, and perfectly colourless when cold. In the inner flame the bead with a small quantity was colourless, with a larger quantity slightly brown when cold.

The mass fused with soda upon charcoal to a glass, which was absorbed by the charcoal, but did not furnish any metallic particles on being subsequently triturated in the mortar. On platinum wire with soda, a reddish-brown transparent glass was obtained while hot,

which on cooling became spotted with brown. In the inner flame a glass was obtained, which remained perfectly colourless, and in which no precipitate was perceptible. Upon heating the bead in the outer flame, the previous reaction appeared.—*Oversigt af. Kongl. Vetensk. Acad. Förhandlingar*, No. III., 1850, pp. 55–61.

On the Constituents of the dry Herb of Cochlearia officinalis. *By* F. L. Winckler.

The same treatment was followed as in the author's former investigation on *Cardamine amara**. This plant contains tannin, as does likewise *Cardamine*, although this was not previously enumerated among its constituents. The aqueous solution of the bitter principle of this plant exhibits the same behaviour as the alcoholic extract of *Cardamine*, and like it furnished with myrosine of yellow mustard, volatile oil of horseradish. The olefiant compound appears to be the same in both plants. The bitter substance from both plants furnishes a compound with basic acetate of lead, which on decomposition with sulphuretted hydrogen, removal of the sulphuret of lead and concentration, yields an acid syrupy liquid, which disengages scarcely any oil with solution of myrosine alone, but immediately and in great abundance with calcined magnesia.—*Jahrb. für Prakt. Chem.*

How to preserve the Protosulphate of Iron from Oxidation. *By* M. Ruspini.

The crystals of the protosulphate of iron are dried as quickly as possible between blotting-paper, and then immediately placed in a drying apparatus heated to 86° F., and the salt allowed to effloresce. In this state it can be preserved in bottles with ground stoppers for any length of time without becoming more highly oxidized.—*Journ. de Chim. Méd.*, vol. vi. p. 197.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Smelting Magnetic Iron Ores. *By* Mr. H. Fairbairn.

Amongst the most interesting objects of observation which are presented to the view of the traveller amongst the iron furnaces and through the iron ore regions of Pennsylvania, none is of more striking importance, in its probable ultimate revolutionary consequences on all the future iron manufacturing of Europe and of America, than the progress towards perfection in the yet imper-

* See Chem. Gaz., vol. vii. p. 421.

fectly established system of smelting the magnetic iron ores of Pennsylvania, or those ores which abound in the primitive rocks in various parts of the state.

Although these iron ores have been hitherto known, in a manufacturing point of view, principally in New Jersey or in Pennsylvania, and only in the region of the Lehigh river, yet the geology of this part of the continent of America displays, in the utmost distinctness, the continuation of the same rocks through a very wide range of country, from north to south—from Connecticut through New Jersey, New York, Pennsylvania, Maryland, Virginia, South Carolina and the south-western states, under various local names. The mountains are of primitive formation, and they are universally non-volcanic—the strata consequently continuous, and unbroken by the mechanical forces which have disturbed the stratification of so large a part of the European countries; and the same iron ores may be reckoned upon as existing almost everywhere throughout the range of the primitive mountains of the United States.

The degradation of the mountains is various, as local circumstances may have produced aqueous decomposition in varying degrees; but this has served the very useful purpose of laying open the deposits of iron in all the stages of geological formation, and it only remains for the manufacturer of iron to choose his location over hundreds of miles of country; or if fuel be absent from any part of the region where a particular iron ore is seen upon the surface, then to dig will be to find (in almost any other situation) the magnetic iron ores, at some depth, however various, between the surface and the granite foundation of the earth.

Scattered furnaces exist throughout Virginia, Maryland, South Carolina and Alabama, and these furnaces are all engaged in the smelting of the magnetic ores of iron; but they are principally charcoal furnaces, on the comparatively petty scale which is that of all iron furnaces dependent on wood for fuel, in this age of colossal competition for the manufacture of the iron of the world at large.

Owing to the circumstance of the existence of the anthracite coal fields in the state of Pennsylvania, and that all the ores of iron exist also in the nearest vicinity to coals and to limestone, it may be stated that the iron ores and the iron manufactures of Pennsylvania are substantially to be the future iron ores and manufactured iron of the United States. Time may develope other modes of smelting, in which coals may not be the all-important consideration; but no extensive manufacture of iron can now exist at any considerable distance from the coal fields of Pennsylvania, however rich and abundant may be the magnetic iron ores of the more southern states. And although, in Pennsylvania, the circumstance of the greater accessibility of the magnetic iron ores in the region of the Lehigh river has hitherto appeared to confine the smelting of these ores to that particular quarter of the state, yet throughout the whole of the region between the Lehigh and the Schuylkill the same ores can be mined where a demand for iron ore exists; and either at Easton on the Lehigh, or at Reading on the Schuylkill, iron furnaces can be

supplied with any quantities, however illimitable, of magnetic iron ores, at an average cost of three dollars per ton.

These ores are the richest of all the ores of iron—not the most productive of iron in the greatest quantities only, but the iron which is thus made from the magnetic ores of the United States is of the finest quality. From the same oxides of iron is produced all the fine iron of Russia, Sweden and Norway—countries which possess primitive geological formations similar to those which occupy a large portion of the state of Pennsylvania; and whilst the search has been made in vain for magnetic iron ores in England, yet in the return to the House of Commons of the importations of iron for the late years of 1848–49, which was made on the motion of Sir John Guest, there is an entry of "1340 tons of chromate of iron from Norway and the United States." There is every variety of iron ore to be found in Pennsylvania, from the richest oxides of Russia to the poorest carbonates of Wales.

But the magnetic iron ores have yet been comparatively useless to the iron manufacturer of Pennsylvania, and Russian and Swedish iron continues to be imported into the United States although made from the same ores as those lying in millions of tons on the granite rocks of the Lehigh. The only instance in which the magnetic oxides have been smelted without admixture with hematite ores is mentioned by Professor Walter R. Johnson in favour of the Stanhope furnaces in New Jersey; and though the work of Professor Johnson is now some ten years old, yet is there no furnace at this time on the Lehigh river where pig iron is produced with any regularity unless mixed with considerably more than one-half of the softer hematite ores. There are occasionally reports of extraordinary success in the attempts which may be made at particular furnaces to smelt the magnetic ores alone; and for a short time there is pig iron in the markets which sells at prices very far higher than the usual anthracite iron, of which there is an instance at this time of such pig iron being sent from a furnace on the Lehigh to Sheffield in England, for the steel manufacture of a place which depends almost entirely on Russia and Sweden for the raw material of steel. Yet this successful smelting of the magnetic iron ores never long fails to be followed by some important damage to the furnace; and it is generally considered that it is not practicable to smelt iron with profit to the manufacturer, when using the magnetic oxides of iron, unless with the admixture of considerably more than one-half of the inferior hematite ore.

But this admixture of inferior ore is fatal to the manufacture of iron on the Lehigh, or elsewhere in Pennsylvania, in competition with the iron of Russia; for the quality of the metal is deteriorated, and the expense is increased, of manufacturing iron from hematite ores, which are usually brought from considerable distances to the furnaces on the river Lehigh. Great quantities of hematite ores are annually sent round from the Schuylkill river to the furnaces in New Jersey, and this ore is sold at an average of one dollar per ton above the magnetic ores, an expense which is most needlessly in-

curred, from a supposed impossibility that the magnetic ores can be smelted alone.

To overcome this difficulty in the reduction of the magnetic oxides of iron is therefore of the utmost importance to the anthracite iron manufacture of the United States. Certain it is that iron equal to that of Russia can be produced from the magnetic ores of Pennsylvania, for the Exhibition of the Franklin Institute exhibited such iron in the late year of 1849; whilst the steel manufactured at the Adirondak works in New Jersey is also from American iron; and the iron recently produced at the largest furnace on the Lehigh river is reported from the rolling mills to be fully equal to Russian or to any other iron, with respect to malleability, but that in the process of puddling a considerable per-centage of its weight has been found to be lost. This latter circumstance may probably lead to the better management of the process of smelting the magnetic iron ores of the United States.

For, against the alleged impossibility of smelting a hard magnetic oxide of iron, there is the refutation in the daily practice of the iron founder, who melts the pig metal itself; and it will not be said that there is any iron ore which is harder than the pig. The practice of the iron founder may therefore point to the true modes of smelting the magnetic ores of the United States.

It is the absence of the waste alone—of three-quarters of the coals, and the limestone—which enables the founder to reduce the metal itself, which yet cannot be produced by the smelter from the much more reducible form of the ore.

There is no iron foundry in which more than 5 cwts. of anthracite coal are used for smelting 1 ton of pig metal; and yet the cupola furnace is blown with cold air, and loses immensely more heat by radiation than is lost from a smelting furnace through walls of many feet in thickness. But the iron founder does not use his coal in enormous lumps, of which the greater part is useless in the smelting process, and lost in the air. Were the cupola furnace filled with lump anthracite coal, 2 tons would equally be required for smelting a ton of pig iron, as a ton of iron from ores which are almost all iron; for there is frequently 90 per cent. of iron contained in the magnetic ores.

But though these ores are almost all iron, and the quantity of earthy adulterations less than in any other iron whatever, yet is there, in the iron furnaces on the Lehigh, no change or shadow of alteration from that everlasting "ton of limestone" which appears to be thrown into every iron furnace in every place and region in the United States. The founder uses only some small portion of lime, a few pounds of oyster-shells being sometimes all that is used for melting a ton of pig metal of impure quality, but more frequently none whatever is used in the cupola furnace; and if the earthy ingredients in the ores be only 10 per cent., or 2 cwt. in the ton, then 1 cwt. of limestone is the true quantity to be used in the smelting furnace, the waste of limestone being one of the leading causes of the unsuccessful attempts to produce iron for steel from the mag-

netic ores of the Lehigh. The unusual waste of iron in the puddling furnace is owing only to the calcareous and carbonaceous concretions which remain from the excessive use of anthracite coals and of limestone in the smelting process, for the loss is not of metal, but of impurities which have been introduced, at a very considerable expense, and only to be again extracted by the further very heavy expense which attends all puddling of iron in the United States.

The chemistry of red short iron may not have been very clearly ascertained, and the phosphoretic substance which Bergman found on the analysis of one kind of iron may not improbably be now sometimes mistaken for calcium or deoxidized lime; but certain it is, in all practical iron manufacturing, that pig iron is rendered more brittle by the excessive use of lime, and this excess is most enormous throughout the iron manufacture of the United States.

In order to illustrate, from actual practice, the undoubted error of using this excessive and unvarying quantity of limestone in the American anthracite iron manufacture, it is here proposed to bring into notice the comparative quantities of limestone and other materials used, formerly and now, in Scotland, and under different temperatures of blast.

At the Clyde iron works, in 1831, the blast at 280° F.:—

	tons.	cwt.
Coal for fusion, 1 ton;—18 cwt. of coke; in coal	4	6
For the hot blast apparatus	0	5
Blowing machine	0	7
Limestone	0	9
In 1833, temperature of blast 612°:—		
For fusion	2	0
Hot air apparatus	0	8
Blowing engine	0	11
Limestone	0	7

Here is seen a reduction of limestone to 7 cwt. per ton of pig iron, at a temperature of 612°, and this quantity is still in use very generally in Scotland, although the limestone of Scotland is only the mountain limestone which intervenes in the bituminous coal measures, and far inferior in quality to the transition limestone of the Schuylkill region, which approaches to almost perfect purity when taken from any low part of the stratum, and usually contains 94 per cent. of pure lime.

That the brittleness of anthracite iron is owing only to errors in its manufacture, is further rendered probable from everything that is known of the quality of the iron produced from hematite ores in other parts of the world. At Ulverstone, in England, iron is made with charcoal from hematite ores, and this iron possesses so nearly the soundness of the iron of Sweden as to be almost equally valuable in the market; nor has it even been doubted that hematite iron ore is second only in value to the magnetic oxides from a lower situation in the primitive rocks. The "ton of limestone" is the greatest mis-

fortune that ever was imported into the manufacturing system of the United States.

Besides the loss of anthracite coal and of limestone, with all the injurious effects upon the metal which so arise from their use in excess, there would seem to be another important error in the filling of the furnaces with the magnetic oxides of iron in an insufficiently reduced state. This variety of iron ore is of a specific gravity proportioned to its great content of pure iron—probably three times heavier than anthracite coal or limestone, or more than double the weight of the hematite or argillaceous iron ore with which it is intermixed so universally at the furnaces on the river Lehigh. The magnetic iron ore will therefore tend to fall, by its greater gravity, through and below the coals, the limestone, and the other ores in the furnace at the same time, lying impressed against the boshes, obstructing the blast, impeding its own reduction, and causing much of the superincumbent coal to be lost to the process of smelting and wasted at the tunnel head. The continual "chills" which occur at the furnaces which use any considerable quantity of magnetic iron ores, are probably to be traced chiefly to that merely mechanical cause. The remedy for this obstruction is very easily to be found by reducing the magnetic ores to the smallest size—as in Sweden the ores are always broken to about the dimensions of an ordinary egg—and by filling also the furnace with the ores more intimately mixed with the limestone and the coals. The expense of the reduction of these magnetic ores to even very minute dimensions, by stamping machinery, would be amply repaid by the facility with which they would be smelted, with the greater quantity of iron which a furnace would produce, and the greater duration of the brick-work of the walls.

The internal form of the furnaces on the Lehigh, which are universally cylindrical, must be viewed as another impediment to the successful smelting of these heavy magnetic iron ores, which will press with increased force, by their greater weight, against the walls of a furnace with an imperfect internal curve. A chill of very great consequential damage has occurred recently at the furnace which was becoming known for the production of iron selling readily at 26 dollars per ton, against the iron of neighbouring anthracite furnaces at 19 dollars per ton, and the furnace in question is of the cylindrical internal form. On the other hand, the Stanhope furnaces are true circles, according to Prof. Johnson; and he mentions, as with exultation, that these furnaces had reduced the magnetic ores without mixture with ores of any inferior kind.

These are the undoubted causes of the unsuccessful attempts to smelt the most valuable of all the ores of iron, the magnetic oxides of the Lehigh region; nor is there any truth whatever in the usual reasoning of the proprietors of iron works, that the use of the hot blast is the cause of the difficulty in the production of iron for the purposes of steel. It has been settled long since, not more theoretically by the extensive series of experiments which were made by

Messrs. Fairbairn and Hodgkinson, for the British Association for the Advancement of Science, than by the daily subsequent experience at all the principal iron works in Scotland, that there is no difference in the quality of iron made by hot air or by cold, or that the difference has been in favour of the hot blast system of smelting, a much larger increase of No. 1 iron having been produced at the Clyde iron works, by the same furnace and from the same materials, after the change to the use of heated air. The opinion that hot blast iron is inferior in quality has long since been exploded at all the iron furnaces of Great Britain; and the hot blast is assuredly not the cause of the inferiority of the great bulk of the anthracite iron of the production of the United States.

By the abandonment of the present very rude and unreasoning modes of building, of filling and of blowing the iron furnaces of Pennsylvania, it would very soon cease to belong to the serfs of Russia to supply the finest of iron from underneath the snows of the Ural mountains, to all the rest of the nations of the modern world. This occupation is very clearly destined to belong to the people of the United States, for all the rarest of the oxides of iron are to be found in the primitive mountains of the Atlantic States; and to use these treasures on some system approaching to the resemblance of mechanical and chemical science is all that would appear to be required for the early and entire ascendency of the iron and steel manufacture of this quarter of the world; for there would be no difficulty in smelting magnetic iron ores were the process conducted on any reasonable plan, and as not only pig iron is reduced daily by the founder, but Russian and Swedish bars, by the manufacturer of steel, and even cobalt (although this is amongst the most refractory of all the metals), it follows that there is no iron ore whatever which cannot be reduced with the greatest comparative ease.

On the supposition that the magnetic ores have only been neglected or disused from causes which the improvement of the general iron manufacture may cause to pass away, then as the deposits of magnetic ores are shown to be boundless for any possible requirement for future manufacturing purposes, a chain of remarkable consequences may be seen to follow the establishment of iron and steel manufactures in the regions of these ores; for not only may the finest of iron be made in any possible quantities in Pennsylvania, but the most valuable of all the varieties of iron may come to be made at a less expense than the worst. 1 ton of magnetic iron ore will produce more metal than 2 tons of ordinary hematite, or than 3 tons of carbonate of iron, whilst the expense of mining the richest will not be greater than the poorest of the ores; and thus may all other smelting become unprofitable in any other regions but those which contain the ores of the original rocks. Russians, Norwegians and Swedes would then cease to be the sellers of all but inferior iron to such nations as Great Britain and the United States; and as the British islands possess a geology not within the probabilities of any deposits of iron ore of a class superior to the hematites, the state of

Pennsylvania and its anthracite coal regions would appear to be destined to take a very high rank in the future manufacture of iron for the world at large.

But this can only be the result of the most œconomical use of the iron ores of the finest quality, since the difference is daily becoming less in favour of any particular nation in any particular pursuit of manufactures or of foreign trade. Navigation is cheapened and rendered more expeditious from year to year, and the freight of commodities is daily lessened over the sea. The difference in favour of the American iron manufacturer would be only the expense of conveying magnetic iron ore from the Lehigh to Scotland or to Wales, as the chromate of iron is now taken to Great Britain from Maryland at Havre-de-Grace, and the cost of the freight is comparatively less. Specimens of both meteoric iron and of specular iron ore were recently shown to the writer by proprietors of iron furnaces on the Lehigh river; and when the non-volcanic character of the region is kept in view, and reflecting that the specular iron ore composes entire hills in the Island of Elba, in the Mediterranean Sea, that the laws of comparative geology render probable the existence of the same ore in continuity of deposit in the places where it has been found at all; consequently that hills of specular iron ore may be found in the regions of the Schuylkill, the Susquehanna, the Lehigh, or any other part of the long line of country which is traversed by the primitive mountains of the United States; and that in the present wasteful use of anthracite coal and of limestone, it might be considerably less expensive to carry the specular iron ore to Scotland than the coals from Pottsville to Reading or the Lehigh;—such considerations render indispensable an equality in the art of smelting iron, in order to the preservation of the local advantage of the possession of the finest of ores. As Scotland, with advantages so inferior, still continues so strangely to supply the lower qualities of pig iron, so will it not be any very long time before the same country will be in possession of the manufacture of the higher varieties of iron, unless upon the rise of a more formidable opposition than any which yet can be discovered in the science of the iron manufacture of the United States. There is no mode of now maintaining an ascendency but by the skill and enterprise of nations. Geology, chemistry and mechanical science are rapidly assisting many nations to become rich from resources which were not formerly supposed to have an existence; and though the position of Pennsylvania is that of so undoubted an apparent magnificence, amidst mineral deposits of so many valuable kinds, yet, without more rapid improvements in their use, neither the magnetic iron ores nor the anthracite coal-fields appear to be destined to increase very materially the wealth and the commercial ascendency of the Republic of the United States.—*Journal of the Franklin Institute*, February 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Presence of Nitrogen in Cast Iron and Steel.
By Prof. R. F. Marchand.

In the manufacture of cast iron from the various ores, a number of conditions intervene, which render it possible that the iron may unite, not only with carbon, but at the same time with a certain quantity of nitrogen. All the combustibles used frequently contain some per cents., or at all events a considerable fraction of a per cent. of nitrogen. The air conveyed by the blast introduces an enormous quantity of it into the furnace, so that it is not surprising to find a pretty considerable weight of nitrogenous compounds as collateral products. Ammonia and cyanogen are frequent constituents of the gases and concretions produced in the furnace. These substances are, it is true, generally formed in a region of the furnace in which the iron, even though already reduced in part, is nevertheless not in a fit state to enter into combinations. The cast iron is formed as such just before the casting; but in this operation it enters into intimate contact with the nitrogenous carbon, and is surrounded by an atmosphere of gaseous nitrogen, which is perhaps here converted, by the presence of the alkaline constituents of the ash and fluxes and of the carbon, partially into cyanogen. The idea therefore that cast iron might contain an essential amount of nitrogen or nitruret of carbon in the form of cyanogen, paracyanogen, mellone, &c., was not at all improbable; and the circumstance, that, as regards steel, it is produced in the finest condition by the action of animal charcoal upon iron, was very likely to lead to the supposition that likewise in this case the amount of nitrogen might be of importance.

The remarkable compound formerly considered to be metallic titanium, and which Wöhler has proved to be a compound of cyanide of titanium and nitruret of titanium, rendered it still more probable that cast iron might equally contain a nitrogenous compound.

Some time ago Schafhäutl asserted most positively that cast iron and steel contained nitrogen, and described the method by means of which he determined the amount, without however communicating the experiments themselves*. Schafhäutl employed Dumas's method of disengaging the nitrogen in a state of gas; and where the

* Phil. Mag. for January 1840, p. 44.

quantity was too small to be measured with certainty, he converted the nitrogen into ammonia by fusing the nitrogenous substance with a mixture of hydrate of potash and baryta, and weighing the ammonia formed as ammonio-chloride of platinum*. In a subsequent paper (article *Steel* in Prechtel's Encyclopädie, p. 364), Schafhäutl communicates the numerical relations which he found in his analyses of steel and iron, but here also the experiments are not given in detail. He found—

	per cent. nitrogen.
In malleable cast iron	0·532
In close-grained cast iron	0·927
In coarse-grained cast iron	0·749
White pig iron	1·200
In Beinhauer's razors	0·532
In steel floss	0·5842

On dissolving steel and other white kinds of cast iron in hydrochloric acid, there remains, according to his statement, a blackish-brown flocculent residue, which, when heated in the open air, burns like tinder, giving off carbonic acid and nitrogen, and leaving a residue of peroxide of iron.

An admixture of ½ to 1 per cent. of nitrogen in iron is so considerable, that it must appear remarkable how it could have been overlooked so long, notwithstanding that Schafhäutl had drawn attention to it, and had pointed out the means of detecting it with certainty. However, if it were possible to overlook 18 per cent. of nitrogen in the titanium of the blast furnaces, this error in the case of iron will not appear so very surprising. The following are the experiments which I had made on this subject some months before Wöhler made known his important discovery. They have since been repeated, for the greater part with the same results.

The test which Lassaigne† proposed for examining a carbonaceous substance for nitrogen, by mixing it with potassium or sodium and fusing it, is beyond all doubt the most sensitive. I mixed some finely-pulverized cast iron with potassium, heated the mixture to redness in the test-tube, exhausted the residue with water, and added to the filtered liquid a solution of the sulphate of the protoxide of iron containing some peroxide, and then hydrochloric acid; a very copious precipitate of prussian blue was formed. Nearly thirty different kinds of cast iron were examined in this manner, and they all showed the same reaction. With steel powder it was still more striking, whilst with soft iron it was never apparent. A mixture of charcoal and pure iron, heated to redness with potassium, gave no cyanogen even when the mixture was extremely intimate, for instance with iron which had been obtained by calcining the succinate or benzoate of the peroxide of iron in a closed vessel. Only once I obtained faint indications of prussian blue on using the residue from some protoxalate of iron.

* Schafhäutl described this method more than a year before Will and Varrentrapp published theirs.

† Chem. Gaz. vol. i. p. 429.

If an excess of potassium is used and ignited with cast iron, it likewise completely prevents the formation of cyanogen; so that, for the success of the experiment, it is best to take a large excess of pure iron powder, and to mix this in the test-tube with small pieces of potassium. There is likewise no production of cyanogen when the mixture is heated in the open air; the conversion of potassium into potash is then too rapid, and this is not effective even at a high red heat, and probably only becomes so at an incipient white heat, when the potash is again reduced by the iron.

When the residue from the reaction, *i. e.* the undecomposed and undissolved iron powder, was washed with water, quickly dried, and heated again with potassium, there was a further production of prussian blue; and this could be continued so long, that with 8 grms. of iron powder I found it impossible to exhaust the reaction.

This considerable amount of cyanide of iron led me to suspect that the source of its nitrogen was not to be sought for merely in the iron, but rather in the atmospheric air, the nitrogen of which was partially absorbed during the reaction. The experiment was therefore repeated in an atmosphere of hydrogen and of carbonic acid.

A test-tube of strong glass, containing the mixture of cast iron and potassium, was closed with a cork having two perforations, through which two tubes were inserted, the one reaching to the bottom of the glass, the other terminating close below the cork. The carbonic acid was introduced at the bottom, the hydrogen from the top, so that the atmospheric air could be easily and entirely expelled. As soon as this was done, the glass was strongly heated, no current of gas being passed through the tube at the time, and the residue treated on cooling exactly as above. When the atmosphere consisted of carbonic acid, a very lively decomposition resulted, and a slow current of carbonic acid had to be passed through in order to prevent any air from entering. In the eighteen experiments made in this manner with some of the kinds of iron previously tested, there was never any immediate production and separation of prussian blue, and only after five or six days was there a very slight, frequently doubtful indication of a blue precipitate at the bottom of the vessel. However much the experiment was varied, both with respect to the kind of iron or steel, the amount of potassium and the degree of heat, the result remained constantly negative. Although it was not probable that the atmosphere of hydrogen or carbonic acid prevented the reaction, supposing it to arise from the presence of nitrogen in cast iron, I nevertheless made the experiment with some animal charcoal and potassium with both gases, and each time there was a copious production of cyanogen. To demonstrate the absorption of nitrogen by a mixture of iron and potassium, it was heated in a glass tube, first passing hydrogen over it in order to remove all humidity, which the already-formed hydrate of potash contained, and adherent naphtha. This must be done with great care. As soon as it had cooled, the hydrogen was replaced by pure nitrogen, and the apparatus closed, so that any change in the volume

of the gas would be perceptible. The mixture was now heated to redness in the atmosphere of nitrogen. After cooling, the nitrogen had disappeared. In two experiments, which gave a different result, it was found that hydrogen and carburetted hydrogen had been formed, the latter from the naphtha. The first heating in the atmosphere of hydrogen had not been sufficient.

These experiments rendered the existence of nitrogen in iron highly improbable; however, it appeared requisite to try the methods employed by Schafhäutl, upon which he based such positive assertions.

10 grms. of finely-filed cast iron from the works of M. Hausmann at Rottleberode, were mixed intimately with 100 grms. of recently-calcined oxide of copper, and treated precisely in the same manner as in the determination of nitrogen in an organic substance. To expel the atmospheric air, carbonic acid was disengaged at the further end from magnesite, which had been previously dried, and the use of which has the advantage that no water is introduced into the combustion-tube; the mixture of oxide of copper and iron was likewise well dried, so that scarcely a trace of water was visible in the delivery-tube. A layer of oxide of copper of 6–7 inches was placed before the mixture, and the tube ten or twelve times pumped out, and filled with carbonic acid. Small quantities of nitrogen were disengaged, which, measured in the moist state at 59° F., amounted to 1·75 cub. centim. As some carbonic oxide might have easily been formed, or decomposition of water have occurred from any adherent moisture, the gas was most carefully examined; but it could not be decreased by mixture with oxygen and passing an electric spark through it, nor on mixing it with an equal volume of explosive gas and detonation. On adding an excess of hydrogen to the oxygen mixed with the gas, the oxygen disappeared on combustion, leaving the original volume of gas undiminished. The gas was undoubtedly nitrogen. Reduced to 32° and a barometric pressure of 760^{mm}, it formed 1·5 cub. centim., or nearly 2 milligrms. (1·89). Admitting the nitrogen to proceed from the iron, 10 grms. would contain about 2 milligrms., or 0·02, in 100 parts. This quantity is 20 times less than Schafhäutl found in the kinds of iron which furnished him with the least quantity.

It was still possible that this small quantity of nitrogen might have proceeded from the apparatus, the mercury, the potash, &c. The experiments were therefore variously modified, and repeated with the greatest care; but it was also possible that the iron might form a compound with nitrogen which might be mixed with the cast iron, and of which perhaps only a small part would be decomposed by the incandescent oxide of copper. The latter was not very likely, as a mixture of cast iron with oxide of copper, in which the latter is not too predominant, takes fire on being heated, and continues to burn with a violent disengagement of gas. If the nitrogen proceeded from the cast iron, and was not the whole of the quantity contained in it, it was possible that the graphite crystallized from cast iron might likewise contain nitrogen. On testing

three kinds of artificial graphite (taking each time 5 grms.), not the slightest production of cyanogen was perceptible, nor was the least trace obtained with native graphite.

I employed the native graphite to obtain an idea of the amount of the error of observation in the above nitrogen determination. 5 grms. were mixed with the same quantity of oxide of copper as had been used for the cast iron, and the arrangement of the entire apparatus was as nearly as possible the same. A few bubbles of an unabsorbed gas were collected over the potash; they amounted to about 0·3 cub. centim., corresponding to about 0·3 milligrm., which, considering them to be also extraneous in the experiment with the iron, must be deducted from the 1·89 milligrm., so that consequently 100,000 parts of cast iron contained 15 parts of nitrogen.

If nitrogen were present in the cast iron, it was possible that it might be concentrated in the carbonaceous matter left on dissolving the iron in muriatic acid. Schafhäutl asserts this positively, and even of white iron. 44 grms. of cast iron from the Rothenberg foundry, in which English iron is cast, were dissolved in hydrochloric acid; it was a beautiful gray iron. It left a residue, which, dried at 302°, weighed 4·008 grms., and contained principally carbon and silicates. The whole amount was burnt with oxide of copper; it furnished 38 milligrms. of nitrogen, which makes 9 parts in 100,000 parts of cast iron. With white cast iron the result was still less in accordance with Schafhäutl's statements. 60 grms. of white cast iron, dissolved in hydrochloric acid, left 0·895 grm. of air-dried residue. When heated to 752°, water and a considerable quantity of a stinking oil were expelled, leaving 0·696 grm. of a substance which had a perfectly white appearance. It was decomposed with soda, after having been freed by treatment with potash from soluble silicic acid, and found to have the following composition:—

Silica	76·72
Protoxide of iron	17·96
Oxide of manganese	1·96
Alumina	0·20
Lime	0·12
	97·06

The loss consisted of a trace of carbon and of alkalies. It appeared superfluous to look for nitrogen in this substance. Nearly the seventh part of the silica can be extracted by potash; the residue therefore appears to consist of free silica, probably of decomposed silicate of the protoxide of iron and inclosed slag ($R^2 O^3, 2SiO^3$).

In several experiments to burn cast iron and steel with oxide of copper, I arrived at the same result as the above. The greatest amount of nitrogen which I obtained was 18 parts to 100,000.

As possibly the nitrogenous compound might have resisted decomposition by oxide of copper, I employed Schafhäutl's second method, decomposition by alkalies. I mixed about 10 grms. of iron with 60 grms. of soda-lime, and examined whether any ammonia had

been formed in the usual manner. In detecting traces of nitrogen by this method, the greatest precaution is necessary, and the neglect of a number of check experiments has without doubt been the cause of many errors. Fresenius has drawn attention to the fact, that the reagents employed in the determination of the ammonia frequently contain ammonia*. I therefore prepared perfectly-fresh hydrochloric acid, used only recently-distilled water, and chloride of platinum dissolved in a large quantity of alcoholiferous æther. The reagents were kept in carefully-stoppered bottles. Nevertheless a certain quantity of these reagents, on being used in the subsequent experiments, furnished so much ammonio-chloride of platinum as left on ignition 0·0006 grm. platinum. With 60 grms. of the soda-lime, which was of the same preparation as that used in all the following experiments, 2 grms. of sugar, 3 grms. of artificial graphite and 5 grms. of native graphite were mixed and ignited; in each of these three experiments nearly 5 milligrms. of platinum were obtained, which appeared therefore to constitute the constant error of observation. No absorption of ammonia during evaporation could have occurred. From these preliminary experiments, it appeared necessary to ascertain whether the presence of the iron did not prevent the production of the ammonia; for supposing ammonia to have been generated, it may easily have been decomposed by the iron or oxide of iron, even in the presence of strong alkalies.

To ascertain the influence of the iron, 6 grms. of the Rothenberg iron were mixed with 0·200 uric acid and 60 grms. of soda-lime, and the nitrogen determined in the usual way. 0·470 grm. platinum was obtained, corresponding exactly to the amount of nitrogen contained in uric acid, viz. 33·37 per cent. From this experiment it follows that iron does not prevent the production of the ammonia, and likewise that it can contain no essential amount of nitrogen.

6 grms. of finely-pulverized Rothenberg iron, used in the same proportions as in the preliminary experiments, furnished 0·0055 grm. more platinum, corresponding to 0·00078 grm., or 0·013 per cent. N.

11 grms. of beautiful gray Rottleberode iron furnished an excess of 0·006 grm. platinum =0·000852, or 0·008 per cent. N.

77 grms. of gray crystallized Malapan iron likewise gave an excess of 0·006 grm. platinum =0·000852 grm. =0·011 per cent. N.

The close coincidence in these three different kinds of iron, with different quantities, rendered it not improbable that the iron took no part in the formation of the ammonia, and that therefore, even with varying quantities, the same amounts of ammonia are obtained; but this coincidence is merely accidental, as will be immediately seen from the following experiments:—

12 grms. Rottleberode iron gave 0·2076 platinum, or 0·0011 N =0·009 per cent.

12 grms. of another piece gave only 0·0026 grm. platinum = 0·000369 N =0·003 per cent.

* This had been previously done by Dr. Kemp. See p. 455, vol. iv. of this Journal.—Ed. *Chem. Gaz.*

10·56 grms. of fine shavings of a good English file gave 0·011 grm. platinum = 0·00156 N = 0·014 per cent.

120 grms. of the same file were dissolved in hot hydrochloric acid; the residue, amounting to 0·287 grm., and consisting principally of earthy silicates mixed with carbon, gave 0·0053 grm. platinum = 0·00047 N.

Besides the above-mentioned experiments, I obtained in six other experiments, with Swedish, English and Mägdesprung iron, exactly the same results. The *possible* amount of nitrogen never exceeded 0·015 per cent.

Lastly, I examined an iron slag from the copper furnace of Sangerhausen, spec. grav. 7·639; it furnished nearly 1 per cent. (0·95) of carbon, and contained a large quantity of molybdenum. 4 grms. gave with soda-lime 0·012 grm. platinum = 0·0018 grm., or 0·045 per cent. N, a much larger quantity therefore than could be obtained from the iron.

It results clearly, in my opinion, from these experiments, that the presence of nitrogen in cast iron and steel cannot be admitted with perfect certainty; at all events it does not amount to 0·02 per cent., and in most cases is decidedly much lower. If nitrogen is present in iron, it evidently belongs to the enclosed foreign substances, which no more enter into the essential constitution of iron than enclosed slag. The iron is so perfectly oxidized by oxide of copper and by soda-lime, that in both cases the whole amount of nitrogen is disengaged.

When iron containing carbon is heated to redness in the air with potassium, nitrogen is absorbed from the air and cyanogen formed. This reaction is the same as that proposed by Thomson for the production of prussiate from the nitrogen of the atmosphere. It requires such a high temperature, that the potash is reduced to potassium, a reaction which undoubtedly occurs in the blast furnaces, and is the cause of the production of the cyanide of potassium in them. In order that its formation may take place, the iron must be chemically combined with carbon; the reaction does not occur if merely mixed with it, unless the temperature is raised so high that cast iron is produced.

The statements of Schafhäutl appear to be founded upon some error of analysis, like those of Buchner, who supposes the presence of sulphocyanogen in an iron from Tyrol, although the presence of sulphur in it is far from being remarkable.—*Journ. für Prakt.*, lxix. p. 351.

On the Odoriferous Principle of the Leaves of Angræcum fragrans. *By* M. Gobley.

The leaves of Faham, known also by the name of Fahon or Fahum leaves, are imported from the Mauritius; they are obtained from a plant first described by Dupetit-Thouars under the name of *Angræcum fragrans*, belonging to the *Orchideæ*. Like many of the exotic Orchids, the Faham is parasitic. It is a charming plant, and

much sought after by the Asiatics on account of its fragrance. It is sufficient to touch the fresh leaves for the fingers to remain impregnated with their aroma. The dry leaves, which occur in commerce, have an odour which considerably resembles that of the Vanilla, belonging to the same family of plants. Alcohol and æther separate the aromatic principle; boiling water removes a slightly bitter principle and a mucilaginous substance, besides the aroma. In the country whence they are derived, and even in France, a very agreeable tea is prepared from them, which is used as a digestive, and even recommended in diseases of the respiratory organs. Mixed with ordinary tea, they impart to it an extremely agreeable perfume.

After numerous experiments, I found the following simple process best adapted for separating the odoriferous principle:—The Faham leaves, reduced to a coarse powder, are placed in a displacement apparatus, and exhausted in the ordinary way with alcohol of 85°. The extract obtained after distilling off the alcohol is introduced into a flask with the quantity of water necessary to give it a syrupy consistence; it is then agitated with æther, which is renewed until it is no longer perceptibly coloured. On evaporating the æther, it leaves a very odoriferous greenish substance. The aromatic principle which it contains is separated by boiling water; the filtered liquid furnishes crystals on cooling, but as these have still a greenish tint, they are purified by recrystallization from boiling water; and lastly, they are completely decolorized by treatment with animal charcoal. The crystals obtained are placed on a filter, when they readily dry in contact with the air.

The aromatic principle of the Faham leaves crystallizes in the form of little white silky needles, or in short prisms terminated by facets; these crystals have an aromatic odour, which calls to mind that of the Faham, and slightly resembles that of bitter almonds and Melilotus. The odour is especially developed by rubbing the crystals between the fingers; their taste is at first slightly bitter, and subsequently pungent. They fuse at about 248° F.; they are scarcely soluble in cold, but readily in boiling water, which deposits them on cooling; they are very soluble in alcohol and æther. The substance to which it approaches most closely is the coumarine, discovered by Messrs. Guibourt, Boutron and Boulley in the Tonka bean (*Coumarouna odorata*), then found in the Melilot (*Melilotus officinalis*) by M. Guillemette, and in the woodruff (*Asperula odorata*) by M. Kosman. The question arose whether these substances were identical.

The odour of coumarine has great resemblance with that of the crystalline substance from the Faham leaves. Both substances are scarcely soluble in cold water, and dissolve readily in boiling water, from which they separate on cooling in acicular crystals; both are soluble in every proportion in alcohol and æther, but they appear to differ in taste, the principle from the Faham leaves being bitter, which is not the case with coumarine. The melting-point would also establish a considerable difference; coumarine is stated to melt at 122° F., whilst the crystalline principle from the Faham leaves

melts at 248°. As the melting-point of substances is an important character, I prepared some coumarine from Melilotus by the same method used for the Faham leaves, and obtained the same identical crystals, which were slightly bitter, and melted at about 248°. The melting-point of coumarine is consequently not 122°, and it must have been masked by traces of the fatty matter, which exists in large quantity in the Tonka bean. With respect to the slight bitterness which the crystalline principles from Melilotus and Faham possess, it is due to a minute trace of a bitter resinous substance, which is found in these vegetables. To prove the complete identity of these two substances, I submitted the crystals obtained from the Faham leaves to analysis, and have compared the results with those obtained by O. Henri with coumarine from the Tonka bean:—

		Henri.
Carbon	76·12	76·40
Hydrogen	4·12	3·99
Oxygen	19·76	19·71

It is evident from this, that the crystalline principles obtained from the Tonka bean, Melilotus, Woodruff and Faham leaves, are the same substance.—*Journ. de Pharm.*, May 1850.

On Chinese Vegetable Tallow, and the Fatty Acid contained in it. *By* J. B. von Borck.

Among the different products of nature and art which the agent of the Swedish government, M. Liljewalch, brought with him from his journey to China, and of which he sent specimens to the University of Lund, was the so-called vegetable tallow, or, as it is chiefly produced in China, Chinese tallow. The fruits accompanied it, from which, according to report, it is prepared, and which were gathered in the presence of M. Liljewalch from a tree about 18 feet high.

A great deal has been written about the preparation of this tallow, which I do not consider necessary to repeat here. I will merely relate what M. Liljewalch states respecting it in his work on the commerce of China (Stockholm, 1848, p. 166):—

"Vegetable tallow, a very light fat so called by foreigners, of which candles are made in China. This substance has the advantage over animal tallow, that the candles made from it neither melt nor smell. The tallow is obtained from a tree called Kau-Shu, which grows over nearly the whole of the low land of China, and the fruits of which (Kintze), resembling a white bean after the shell has been removed, furnish on pressure two products, one liquid like oil, the other hard like tallow. I have never met with the oil in commerce; the tallow, on the contrary, is an important article of commerce in China, and varies in goodness; that produced in the neighbourhood of Canton is neither so hard nor so white as that from the province Chejang. Ningpo is the right place to buy at; the price, 8 to 9 dollars per picul (133⅓ English pound)."

Osbeck saw the tallow-tree in 1750–52. According to him, the tree was called O-ka-o, is only 6 feet high, and grows in the neighbourhood of water. M. Liljewalch mentions, in a letter to Prof. Berlin, that it is not impossible, considering that the tallow produced in North China is harder, and also that the harvest takes place there in October, whilst in Southern China the fruit is already ripe in June and July, that two different kinds of the tallow-tree are cultivated. Osbeck, who visited only the southern part of China, would, according to this, have seen a different tallow-tree from that seen by Liljewalch. However, the difference of the tallow may be explained by the different position of the land, and also by the different modes of preparation.

The tallow obtained from M. Liljewalch, which furnished the material for the present investigation, forms a square mass of a white colour, without odour or taste; it was scarcely fatty to the touch, but almost dry, and was uncommonly light; its specific gravity at 54° F. was 0·818. It melted at 99°, began to congeal at 86°, but did not become perfectly hard before 72°. The tallow dissolved readily in æther, only slightly in cold alcohol, but in about 75 parts of boiling alcohol of 0·82, from which it was deposited on cooling as a granular mass. A liquid fat was left in the mother-ley, but the granular fat had the same melting-point as before. A fatty acid was separated by saponification, which, after crystallization from alcohol, possessed the constant melting-point, 61°–62°.

The fruit appeared to belong to *Stillingia sebifera*, Mich. (*Croton sebifer*, L., *Ricinus Chinensis*, Petiv.). They are seated in threes on the *columna centralis*, which is divided into three parts, and surrounded by the trilocular deciduous seed-capsule. Each fruit is from 3 to 5 lines long, broadly ovate, strongly convex on the outer side, but on the inner, where the fruit was seated together, angularly flattened. It is properly speaking a stone-fruit, the kernel of which is surrounded by a hard, brownish-black shell; this shell is clothed with a thin (about $\frac{1}{4}$th of a line) snowy white layer, consisting of cellulose containing the deposited fat. According to an approximate determination, the fruit consists in 100 parts of—

Kernel	38
Shell	37
Layer of fat	25

From the pounded kernels, about 65 per cent. of a mild reddish-yellow fatty oil could be obtained by means of boiling alcohol.

No tallow could be separated from the cellulose by boiling with water; but boiling alcohol of 0·803 extracted a fat, which on cooling was deposited in the same manner as the Chinese tallow; the melting-point was 104°, but by recrystallization it was brought to 118°. A fatty acid was separated by saponification, which perfectly resembled the acid from the tallow, and possessed the same composition. This will, I think, place the origin of the tallow beyond doubt. The low melting-point of the tallow may easily be explained from the mode of preparation, in which it was not possible to avoid a mixture of the liquid oil of the kernels.

To examine the fatty acid, the tallow, after being purified by alcohol, was saponified with potash, which was very readily effected, and the soap twice separated from its solution in water by a saturated solution of chloride of sodium. The soap was then decomposed at a gentle heat with dilute hydrochloric acid, and the separated acid washed with water. It formed a hard crystalline mass, which melted at 131°. By recrystallization from hot alcohol, I obtained an acid, the melting-point of which was at 142°–144°. As this melting-point was not altered by frequent recrystallization, and remained the same for the acid from the tallow which melted at 99°, from the tallow of the fruit-shells which melted at 118°, and lastly from the stearine which had been prepared with æther, and whose melting-point was 140°, I have admitted that the acid does not consist of a mixture of several fatty acids, but is distinct. From the alcohol which had deposited the fatty acid, I was able to obtain a liquid oleic acid. The alkaline solution, after saponification of the tallow, contained glycerine, the presence of which in the tallow was also proved by the odour of acroleine on the application of heat.

The fatty acid has the following properties:—It dissolves very readily in hot alcohol, and crystallizes on cooling in beautiful pearly laminæ, which are the larger the more water the alcohol contains. It dissolves with greater difficulty in cold alcohol, but readily in æther; its melting-point is situated between 142° and 144° F., and its point of solidification is the same. When heated to 482°–572°, the acid is not altered; it again solidifies in a crystalline state, and has the same melting-point as before. At a higher temperature the acid distils over unaltered.

At 212° it does not lose in weight. The dried acid gave, on being burned with chromate of lead—

Carbon	74·29	74·45	74·17	74·53	74·19	30 = 2253·6		74·41
Hydrogen	12·70	12·68	12·48	12·38	12·46	30	374·4	12·37
Oxygen	13·01	12·87	13·35	13·09	13·35	4	400·0	13·22

leading to the formula for the crystallized acid, $C^{30}H^{30}O^4$.

The amount of water of the acid was determined by the loss which it experienced on being melted with well-dried finely-powdered oxide of lead. 0·7323 grm. of the acid lost 0·0275. The crystallized acid consists therefore of—

	Found.	Calculated.
Anhydrous acid.....	96·26	2915·52 = 96·29
Water	3·74	112·48 3·71

The formula $C^{30}H^{30}O^4$ belongs, according to Walter, to benic acid, which is contained in the oil from the fruit of *Moringa aptera*, along with margaric, stearic and moringic acid. But benic acid is readily soluble in cold alcohol, crystallizes in verrucous masses, and melts at 126°–128°; it cannot therefore be identical with the acid under examination. But, on the other hand, the fatty acid of the Chinese tallow resembles margaric acid in many respects. It crystallizes exactly like it, distils unaltered, and furnishes an ethyle compound closely resembling margaric æther. Besides the difference of composition found by analysis, these two acids are distinguished,

although but slightly, by the melting-point; and from the fact, that the compound of the new acid with the oxide of lipyle, in the purest state possible, melts at 140°, which margarine never can be brought to; and that the lead salt of the new acid melts at 234°, whilst margarate of lead melts at 342°.

In composition the acid of the Chinese tallow approaches very closely to the palmitic acid; the latter contains, in the hydrated state, 0·63 per cent. carbon and 0·10 per cent. hydrogen more. It was possible that in the combustion of the acid I had obtained too little carbon, and that the two acids have the same composition; and, in fact, the silver salts furnished results which corresponded better with the formula $C^{32}H^{30}O^3$ (anhydrous palmitic acid) than with the formula $C^{30}H^{29}O^3$. But since other compounds corresponded well with the latter formula, and the above salt was not easy to obtain perfectly pure, I have admitted the formula above given. That the two acids are decidedly not identical is evident among other things from the fact, that the acid of the Chinese tallow is not in the least altered by exposure to the air at 500°, whilst palmitic acid would have become converted under such circumstances into palmitonic acid.

The fatty acid of the Chinese tallow is consequently new, and I propose for it the name of *stillistearic acid.*

Stillistearine.—It has already been mentioned, that the tallow, which melts at 99°, is deposited, on recrystallization from hot alcohol, as a white granular mass, whilst a liquid fat remains in solution; but by repeated recrystallization, the melting-point can be scarcely raised. The melting-point of the tallow from the shells, which contains less oil, can be brought by recrystallization to 118°, but not further. However, a stearine can be obtained from the tallow by crystallization from æther, which does not melt below 140°; it is nevertheless not free from elaine, for the acid separated from it does not attain the melting-point of 142°–144° before recrystallization. The quantity of elaine is however very small. The stearine was burnt with chromate of lead, when it gave—

Carbon	75·68	75·38	33	= 75·88
Hydrogen	12·13	12·13	31	11·85
Oxygen	12·19	12·49	4	12·27

or 1 equiv. oxide of lipyle, C^6H^5O, combined with 1 equiv. anhydrous acid, $C^{30}H^{29}O^3$.

Stillistearate of Soda was prepared by digesting the acid with weak soda-ley. An almost transparent pasty liquid was obtained, which on cooling solidified to a mass of long slender silky needles. The salt dissolves in 10 parts of boiling alcohol; the solution forms a jelly on cooling, in which after some hours signs of crystallization appear. From a solution which contains more alcohol, iridescent acicular crystals are immediately deposited; the salt forms with a little water a clear solution, which on the addition of more water becomes turbid, and deposits an acid salt.

Stillistearate of Lead is easily prepared by melting the acid with

oxide of lead, rubbed to a fine powder, and removing the excess of acid by æther. The salt forms a wax-like white mass, which melts at 234°, and is nearly insoluble in alcohol and æther. Its composition is—

Acid	67·82	67·65
Oxide of lead	32·18	32·35

Stillistearate of Silver.—The alcoholic solution of the soda salt, mixed with an alcoholic solution of nitrate of silver, gave a white caseous precipitate, which was easily obtained pure by washing with hot alcohol; whilst moist, this precipitate soon blackens by exposure to the light; this decomposition proceeds more slowly when it is dry. It forms a fine light powder, dissolves in a hot solution of ammonia, and is again deposited on cooling in indistinct scales.

The analytical experiments with this salt did not furnish perfectly satisfactory results, owing probably to the difficulty of obtaining it pure and of constant composition; it gave—

Carbon	52·59	52·11	30	= 51·64
Hydrogen	8·58	8·72	29	8·30
Oxygen	..	..	3	6·86
Oxide of silver	32·39	..	1	33·20

Stillistearate of the Oxide of Ethyle was prepared in the usual way, by passing hydrochloric acid gas into an alcoholic solution of the acid. This æther closely resembles margaric æther; it melts at 72° to an oil, but solidifies on cooling to a crystalline mass. At a higher temperature it distils over unaltered. In the analytical experiments made with it, I have not been able to obtain accordant results, and want of material has prevented me from proceeding further with the subject.

P.S. This paper was already written before I became acquainted with R. D. Thomson and Wood's investigation*, according to which the fatty acid of the Chinese vegetable tallow is margaric acid mixed with a small quantity of stearic acid. The acid which they examined melted at 154°; they must therefore have examined a different kind of tallow to that which served as material for my investigation, for I was never able to raise the melting-point of the acid described by me above 144°.—*Journ. für Prakt. Chem.*, xlix. p. 395.

On some Compounds of the Metallic Chlorides with the Perchloride of Cyanogen and Hydrocyanic Acid. By L. Klein.

The existence of the compounds of the perchloride of titanium with the perchloride of cyanogen and with hydrocyanic acid, recently described by Prof. Wöhler, rendered it probable that some other chlorides might form similar compounds, and led the author to make the following experiments:—

Perchloride of Tin and Hydrocyanic Acid.—Perchloride of tin

* Phil. Mag., vol. xxxiv. p. 350.

and anhydrous prussic acid, mixed with each other, combine with great energy, but without any perceptible evolution of heat, evidently owing to the production of a compensating amount of cold by the rapid evaporation of prussic acid and of the compound produced. This compound is a solid crystalline body. It is obtained in beautiful crystals when gaseous prussic acid is passed into perchloride of tin, presenting a large surface in a tube. The chloride becomes heated to about 86°, at which temperature the new compound volatilizes. It then forms colourless, transparent, highly-refractive crystals, which appear to be isomorphous with the corresponding compound of titanium. It appears to be quite as volatile as anhydrous prussic acid, and evaporates as quickly in a current of dry air, the crystals becoming white and opake. The same occurs in the vapour of prussic acid. It fumes considerably in moist air, and is decomposed with evolution of prussic acid. With water this takes place with disengagement of heat. It unites with ammoniacal gas, with considerable evolution of heat, to a white sublimable body.

On account of its great volatility, I was unable to ascertain its quantitative composition with certainty. It is probably identical with that of the analogous titanium compound, viz. $HCy + SnCl^2$.

The perchloride of tin does not appear to enter into combination with the perchloride of cyanogen.

Perchloride of Antimony and Hydrocyanic Acid.—The combination of these two substances takes place with considerable energy, the two liquids solidifying to a white crystalline mass. The compound is obtained more distinctly crystallized in transparent prisms, by passing the vapour of anhydrous prussic acid into perchloride of antimony heated to 86°. It volatilizes between 158° and 212°, but with partial decomposition, prussic acid being set free, and a white mass, which subsequently turns yellow and then brown, is left behind. It could not be volatilized entirely undecomposed in a current of carbonic acid. It does not fume in a moist atmosphere, but deliquesces. Water separates antimonic acid. It absorbs ammoniacal gas, and is converted into a dark, pulverulent, brownish mass.

For analysis, some perchloride of antimony was saturated in a weighed apparatus with prussic acid, and the excess of the latter expelled by dry air. 4·199 grms. of the compound were obtained, which were dissolved in water containing tartaric acid, and precipitated by a current of sulphuretted hydrogen; 2·231 persulphuret of antimony were obtained, corresponding to 3·264 of the perchloride of antimony. The compound is consequently $Sb^2Cl^5 + 3HCy$, and consists of—

Perchloride of antimony	77·74	79·07
Hydrocyanic acid	22·26	20·93

Perchloride of Antimony and Perchloride of Cyanogen.—When gaseous chloride of cyanogen is passed into the perchloride of antimony, it becomes slightly heated, turbid, and filled gradually with slender crystals. When saturated, the compound forms a finely-crystalline white mass. It can only be partially sublimed without decomposition, the greater portion parting with the chloride of cya-

nogen. It is immediately decomposed by water. It combines with ammoniacal gas with evolution of heat, forming a yellow pulverulent substance.

2·785 grms. of the perchloride of antimony absorb 0·466 perchloride of cyanogen, according to which the compound would contain 14·06 per cent. of the latter. A combination of the chlorides in equivalents would consist of—

Perchloride of antimony.....	83·28
Perchloride of cyanogen.....	16·72

It was undoubtedly not perfectly saturated with perchloride of cyanogen.

Perchloride of Iron and Hydrocyanic Acid.—Sublimed chloride of iron, when mixed with anhydrous prussic acid, combines with a hissing noise, and dissolves with a reddish-brown colour in the excess of acid. The liquid soon congeals to a brownish-red crystalline mass, from which the excess of acid can be expelled by heating to about 86° or under the air-pump.

The compound forms minute, shining, reddish-brown, crystalline scales, which quickly deliquesce in the air, giving off prussic acid. The same decomposition is instantly produced by water. At 212° the compound fuses, but also with loss of prussic acid. It combines with gaseous ammonia with evolution of heat, to a greenish-black powder, which dissolves in water with separation of prussian blue, and must consequently contain protochloride of iron. When heated, it furnishes ferruginous chloride of ammonium, prussic acid, and a residue of protochloride of iron.

For analysis, 1·168 grm. of the compound was dissolved in water, the prussic acid expelled, and the iron precipitated by ammonia. 0·427 peroxide of iron was obtained, corresponding to 0·867 perchloride. According to this, the compound is $Fe^2Cl^3 + 2CyH$, and consists of—

Perchloride of iron.....	74·23	75·04
Hydrocyanic acid	25·77	24·96

Perchloride of Iron and Perchloride of Cyanogen.—Sublimed perchloride of iron absorbs chloride of cyanogen with evolution of heat, and melts to a black mass. I was unable to obtain this compound perfectly saturated. On the application of heat, it melts with tumescence and loss of chloride of cyanogen. It is worthy of remark, that solid chloride of cyanogen is obtained sublimed in crystals.—Liebig's *Annalen* for 1850.

On the Constitution of Styracine. By Dr. A. Strecker.

I recently advanced the view*, based upon the experiments of M. Toel†, that styracine is a compound of *cinnamic acid* with the *alcohol of cinnamic acid* (styrone). All the facts related by M. Toel and the analyses of the different products agree well with the formulæ proposed by me, with the exception of the analyses of styracine, which in part at least accord better with M. Toel's formula.

* Chem. Gaz., vol. vii. p. 272. † Ibid., p. 249.

To get information on this point, I prepared some styracine, and obtained it perfectly pure by repeated crystallization from alcohol and æther. It possessed all the properties ascribed to pure styracine by M. Toel. After drying over sulphuric acid, it was burnt with chromate of lead, when it gave—

Carbon.....	81·47	81·37	36 = 216		81·82
Hydrogen	6·09	6·06	16	16	6·06
Oxygen	..	..	4	32	12·12

The slight loss in carbon was to be expected in the combustion of a substance so rich in carbon, unless oxygen were employed; the principal object however was an accurate determination of the quantity of hydrogen, which according to the formula $C^{36} H^{14} O^3$ should amount to 6·42 per cent. I think therefore that the formula $C^{36} H^{16} O^4$ for styracine may be considered as established.—Liebig's *Annalen*, April 1850.

On the Residue obtained on dissolving Pig Iron. *By* Prof. Wöhler.

Prof. Schafhäutl had observed that the carbonaceous residue left on dissolving gray pig iron in muriatic acid, after perfect exhaustion with acid and edulcoration with water, exhibits a lively disengagement of hydrogen gas when ammonia is poured over it. This remarkable behaviour has been completely confirmed by M. J. Hull; but, according to his experiments, it is owing to a purely mechanical cause. The hydrogen evolved is contained mechanically inclosed in the porous carbon, and is expelled from it not merely by ammonia, but also on heating the residue with pure water. That it is disengaged by ammonia at the ordinary temperature is probably owing to the circumstance, that the ammonia by dissolving the oily hydrocarbon, immediately penetrates and moistens the carbonaceous mass.—Liebig's *Annalen*, April 1850.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Beet-Root Sugar without the Employment of Animal Charcoal. *By* Dr. Lüdersdorff.

In the manufacture of beet-root sugar, the employment of animal charcoal may, according to M. Melsens, be dispensed with, by the application of sulphurous acid or its acid salts; any other acid will however answer the purpose; but, as will easily be understood, such other acid will be preferred as admits of being readily driven off, as it is found to be a matter of difficulty to deprive the sugar so completely of sulphurous acid as to leave no traces of its smell.

M. Lüdersdorff had occupied himself with this subject as far back as 1837, and succeeded in discovering a process for preparing, with-

out the use of animal charcoal, not only beet-root syrup of excellent quality, but also molasses. He states, that he solicited a patent for this process in 1838, but did not follow it out, as at that time the cultivation of beet-root in the environs of Berlin presented no sufficient advantage over other substances. From the impetus recently given, however, to the manufacture of beet-root sugar, M. Lüders dorff thought it might be useful to make the process more generally known, especially as the agent employed by M. Melsens, although attended with serious objections, had given rise to the most brilliant expectations. M. Lüdersdorff therefore furnishes the following explanation of the process by which he imagined he could obtain a satisfactory result, of the nature sought by M. Melsens, and in fact partially secured by that gentleman, by the employment of sulphurous acid.

It is well known that beet-root juice is very rapidly oxidized; although colourless when in the root, it acquires, in a few moments after being expressed from the pulp, an intense black colour; and soon afterwards, in consequence of the presence of secondary nitrogenous products, viscous fermentation takes place, which not only (if not stopped) would continue until the whole of the sugar was destroyed, but which, even if stopped, renders it extremely difficult, if not impossible, to extract the sugar still present. This appeared to be worthy of attention and experiment, especially as it was attended with another singular phænomenon, viz. that on subsequent purification by means of lime, the black colour of the juice became changed to an intense yellow, which by concentration passed to a deep brown, thus rendering the employment of animal charcoal necessary. The prevention of the oxidation of the juice appeared therefore to be the first result to be obtained.

Independently of this, a further examination of the juice showed that the extraneous matters it contains were divisible into two classes, which have somewhat the character of positive and negative in relation to each other. By the employment or contact of an *acid*, only a portion of these concomitant matters is coagulated, whilst the others can only be eliminated in a concrete form by means of an *alkali*, such as lime. According to the present plan of defecation, lime only is employed. It is therefore evident that the positive extraneous matters in the juice not only remain there, but are, by the ulterior action of the lime, changed into bodies which are no longer susceptible of being coagulated. The elimination of each of these classes of substances, taken separately, therefore appeared to be the second problem to be solved. Now, to prevent the oxidation of the juice, any mineral acid may be employed. Of these bodies, sulphuric acid appears to be the best suited for the purpose. It is however to be regretted that phosphoric acid cannot be employed by reason of its high price, as the possibility of its entire elimination would greatly facilitate the following operations. Sulphuric acid has therefore been preferred.

On mixing with the pulp, freshly rasped, $\frac{1}{2000}$th part of its weight of concentrated sulphuric acid, all oxidation will be prevented, the

pulp will remain as white as the beet-root itself, and the juice expressed from it will be of a milk-white colour. It has also been found, that by the employment of the acid, the quantity of juice obtained from a given quantity of pulp is increased.

The juice thus obtained possesses, as above mentioned, a milky appearance. This cloudiness is occasioned by a light precipitate in the liquid, which deposits very slowly, and consequently requires some medium to carry it down. For this purpose plastic clay is found to answer. About 3 per cent. of this substance, mixed with the juice, will suffice to throw down the precipitate; and at the end of twelve hours two-thirds of the juice will have become as limpid as water, and the whole may be reduced to the same state by filtration. Although, in the space of twelve hours, the action of the sulphuric acid upon the crystallizable sugar was not perceptible, yet it appeared advisable to shorten the duration of its action as much as possible. No other precipitating agent has however been discovered, by means of which the acid juice can be clarified even by careful filtration.

In the means of preventing the oxidation of the juice, has also been found, not only that which, like all mineral acids, forms an obstacle to viscous fermentation, but also that by which the elimination of the positive extraneous matters may be effected. The same acid, and moreover the same quantity, is sufficient to stop the fermentation on the one hand, and on the other effects the elimination. Now in order to separate the negative matters from the juice, it is sufficient to have recourse to the ordinary operations of defecation by means of lime. For this purpose, the acid juice is neutralized by means of milk of lime, and after heating the juice the necessary quantity is added for the purpose of effecting the defecation. M. Lüdersdorff states, that much less time is consumed in this process than in the ordinary defecation of blackened juices, and that the filtration is much more rapid.

The juice obtained after this latter defecation is not absolutely colourless, but has still a yellow tinge. During the boiling which follows this operation, before crystallization, the colour is very little deepened, so that a very white sugar is obtained without employing the least portion of animal charcoal. With respect to the first syrups, they furnish a full fourth of sugar very easily. It will thus be seen that sulphurous acid, the employment of which is so disadvantageous, can be dispensed with, and good sugar obtained without the use of charcoal, as sulphuric acid, judiciously applied, has precisely the same effect. It must not however be forgotten that the employment of this acid is attended with many disadvantages; amongst others, the difficulty of extracting the sulphate of lime in boiling down the clarified syrup, and especially the clarification of the acid juice, which is effected very slowly. It cannot be denied that this is a serious evil; but supposing that by perseverance this difficulty is overcome, there still would remain another question, viz. whether the temperature of 75° C., at which the filtration of the juice takes place with rapidity, has not an injurious influence upon the sugar?

Lastly, it remains to be ascertained whether phosphoric acid could not be manufactured sufficiently cheap to be employed in place of the sulphuric acid, in which case all the above-mentioned difficulties would disappear.—Newton's *Journal*, July 1850.

Method of hardening Objects in Plaster of Paris, and rendering them like Marble.

Take 2 parts of stearine, 2 parts Venetian soap, 1 part pearlash, and 24 to 30 parts of solution of caustic potash. The stearine and the soap are cut into slices, mixed with the cold ley, and boiled for about half an hour, constantly stirring. Whenever the mass rises a little cold ley is added. The pearlash, previously moistened with a little rain-water, is then added, and the whole boiled for a few minutes. The mass is then stirred until cold, when it is mixed with so much cold ley that it becomes perfectly liquid, and runs off the spoon without coagulating and contracting. Before using this composition, it should be kept for several days well-covered. It may be preserved for years. Before applying it to the objects, they should be well-dusted, the stains scraped away, and then coated by means of a thick brush with the mass as long as the plaster of Paris absorbs it, and left to dry. The coating is then dusted with leather or a soft brush. If the surface has not become shining, the operation must be repeated.—*Archiv der Pharm.*, lvi. p. 327.

PROCEEDINGS OF SOCIETIES.

Royal Society.

April 18, 1850. (The Earl of Rosse, President, in the Chair.) The following paper was read:—

"On the Oils produced by the Action of Sulphuric Acid upon various classes of Vegetables," by John Stenhouse, Esq., F.R.S.

Nearly thirty years ago Döbereiner observed, when preparing formic acid by distilling a mixture of starch, peroxide of manganese and sulphuric acid, that the liquid which passed into the receiver contained a small quantity of oil which rendered it turbid. To this oil Döbereiner gave the fanciful name of "artificial oil of ants," though the very limited quantity in which he was able to procure it prevented him from determining almost any of its properties.

The author's attention was first directed to the subject in 1840, when he found that the oxide of manganese was unnecessary, and that the oil could be readily prepared by operating on most vegetable substances with either sulphuric or muriatic acid. The oil, on analysis, was found to have the formula $C_{15}\ H_6\ O_6$, and to contain oxygen and hydrogen in the proportions to form water, while all other oils and fats contain an excess of hydrogen.

The late Dr. Fownes took up the subject in 1845, and made the

interesting discovery, that when the oil which he called furfurole is heated with ammonia, a crystalline amide is formed. When this amide is boiled with caustic lyes, it is changed into the crystallizable base furfurine. The paper then describes the best mode of preparing furfurole, and also the method of purifying it from an oil with which crude furfurole is always accompanied, and to which the name of meta-furfurole has been given. Meta-furfurole is the cause of the bright red coloration which impure furfurole instantly produces when it is treated with muriatic or sulphuric acids in the cold. This portion of the paper concludes with some new observations on furfurole, and an examination of some of the salts of furfurine.

It has been pretty satisfactorily ascertained that the constituent of plants which yields furfurole is the *matière incrustante* of M. Payen, viz. the matter with which the interior of the cells of plants is lined. This is an amorphous granular substance which has been gradually deposited from the sap in its passage through the tissue of the plant. It is most abundant in hard woods, such as oak and teak, especially in the oldest portions which lie nearest the heart of the tree. As the author of the paper was led to conjecture that the *matière incrustante* of the different great classes of vegetables would be found on examination analogous but not identical, he thought it likely that the oils derivable from them would also prove not identical with furfurole, though probably very analogous to it in their nature and properties. The algæ or sea-weeds, whose structure is very different from that of ordinary herbaceous plants, were employed to test the truth of this hypothesis. They yielded an aromatic oil to which the name of fucusole was given. Though essentially different from furfurole, it closely resembles that oil in its properties, being also isomeric with it. Fucusole forms a crystallizable amide with ammonia, called fucucamide, which, when it is boiled with alkaline lyes, is also converted into an organic base—fucusine, which is likewise isomeric with furfurine. Fucusine is a rather difficultly crystallizable base; but some of its salts, especially the nitrate, may be readily procured in large crystals. In solubility and crystalline form they differ from those of the corresponding base.

The paper contains an analysis of these salts.

The mosses and lichens were also found to yield fucusole. The ferns, on the other hand, yield a peculiar oil, which differs both from fucusole and furfurole, possessing properties intermediate between them.

The results of these experiments seem to indicate some curious botanical relations, as it appears highly probable that the *matière incrustante* is the same in all phanerogamous plants, as they yield furfurole. On the other hand, the *matière incrustante* in the Algæ, mosses and lichens, as it yields fucusole and not furfurole, though the same in each of these classes, is evidently different from that of phanerogamous plants. The *matière incrustante* of ferns appears however to be dissimilar from either of the others, as it yields an analogous but peculiar oil.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Mercurial Ointment and the Vapour of Mercury. *By* F. von Bærensprung, M.D.

I. Notwithstanding the daily employment of mercurial frictions, the question of the manner in which the action takes place has but seldom been taken up. The metallic mercury contained in the blue ointment must necessarily penetrate the epidermis and corium, to come into contact with the blood and the internal parts of the body. Animal membranes are permeable to liquids; mercury is a liquid; hence there would scarcely be any doubt *à priori* that this penetration is possible. It has already been shown by Béclard and Krause, that liquid mercury cannot penetrate the epidermis even when subjected to a perpendicular pressure of 26 inches; but the extremely finely-divided state in which it exists in the ointment might possibly present a favourable condition for endosmosis. Hence I first made some experiments with dead animal membranes. A pig's bladder was stretched over a vessel, and blue ointment rubbed upon it for a quarter, half, one, and even several hours; the ointment never disappeared entirely, but there remained at last a tenacious bluish-gray layer on the surface. When the friction was concluded, the under side of the bladder was examined with the microscope; and with a clean piece of gold. Globules of mercury can be readily detected under the microscope in the form of spherical corpuscles, appearing perfectly black and opake by transmitted light, but exhibiting by reflected light a bright white and shining luminous spot. Gold is at least an equally delicate test from its power of forming an amalgam; and a globule of mercury which is barely perceptible to the naked eye produces a distinct white speck upon a piece of gold. In the numerous experiments which were made, however, both methods always yielded a negative result; neither in any case could a trace of the metal be detected between the coats of the bladder on stripping them off; nor was a different result subsequently obtained, whether the friction was performed upon the porous or the mucous surface, or whether a dry or wetted bladder was used, or one impregnated with fatty matter. It was therefore repeated with the more delicate bladder of the calf and sheep; and lastly, with the peritoneal coat of the liver of a calf, a membrane so thin that the smallest print can be read through it; but in this case

the piece of gold which had been enveloped in it did not exhibit any spot, nor did the microscope detect any globules.

But the structure of the human skin and that of animals is different from that of the serous and mucous membranes; and it might be considered possible that the mercurial particles were rubbed into the orifices of the hair-cavities, the sebaceous and sudoriparous glands, and were thence taken up into the capillary vessels. But it is incorrect to imagine that the above organs are open canals; they are perfectly filled with cells, which exactly resemble the cells of the epidermis; moreover, direct experiments have proved this view to be untenable. When the friction was made upon a piece of human skin, or that of a cat or rabbit, mercury could never be detected on its inner surface; and microscopic examination showed that the ointment had penetrated into the external orifices of the follicles, but never further into them.

These facts undoubtedly show that metallic mercury cannot permeate dead animal membranes endosmotically. The laws of endosmose apply equally to dead and living bodies; still it appeared worth while to obtain distinct proof in regard to the latter. ½ a drachm of mercurial ointment was therefore daily rubbed into the skin of a rabbit which had been carefully shaved, until the tenth day, when the animal died with the symptoms of mercurialism. The inner surface of the skin, after having been carefully separated, and the blood and all the more important organs, were most minutely examined; but the result was in nowise different. The same experiment was performed upon several other rabbits, dogs and a cat, all of which shortly died of mercurialism; but in no case could the least trace of metallic mercury be detected in the body.

The ingenious experiments of Autenrieth and Zeller, who first caused the skin to cicatrize over pieces of gold inserted beneath it, and then rubbed mercurial ointment upon it, and on subsequent examination found them unaltered, were long ago attended with the same result; this was however controverted by Œsterlen, who rubbed the ointment into dry membranes and the skin of living animals, and states that he always found numerous globules of mercury, not merely in and under the skin, but in almost all the organs, tissues and secretions. With regard to this point, it must be remarked, that, unless the most scrupulous care be taken in cleaning the hands, the knife, the object-slide, &c., globules of mercury may be found wherever they may be looked for. If we consider, moreover, that Œsterlen also found that powdered charcoal passed by absorption from the intestine into the lacteals, we shall be justified in doubting the accuracy of these experiments, and giving the preference to my experiments.

Since it has therefore been shown, that the metallic mercury in mercurial ointment does not pass into the body as such, it remains to be shown in what other manner this passage takes place.

When mercurial ointment is melted in a test-glass, the metal separates from the fat, so that the former constitutes a white layer at the bottom of the glass, whilst the latter forms a yellow super-

natant liquid; whilst between the two there is a thin black stratum, which appears thinner when recently-prepared ointment is used, and deeper when the ointment is old. This is also seen when the metal is separated from the fatty matter by solution in æther. Hence, in addition to metallic mercury and fatty matter, the ointment contains a black substance, the quantity of which increases with its age; it is also a well-known fact, that the ointment gradually gets darker by keeping. It was natural to regard this black matter as protoxide of mercury, the formation of which is favoured by the absorption of oxygen occurring whilst the fatty matter was becoming rancid. That this was the case could be proved by the following experiment. Some freshly-prepared ointment was treated with æther, the solution poured off; the metallic residue was washed with æther, and then treated with water to which a few drops of sulphuric acid had been added. The acid, which was cold and very dilute, could not attack the metallic mercury, but would dissolve any oxide which was present. A few drops of solution of sulphuretted hydrogen were added to the filtered solution, when a brown turbidity immediately appeared, which after some hours had subsided in the form of flakes. When, instead of the fresh ointment, some which had been longer kept was used, the same reaction appeared much more strongly, and a distinct precipitate of sulphuret of mercury was formed.

In another experiment, acetic acid was substituted for the sulphuric acid. The result was the same. *It is thus proved that mercurial ointment contains protoxide of mercury in addition to metallic mercury and fatty matter**.

Donovan and Christison long since asserted this to be the case, but the younger Mitscherlich rendered it again doubtful. The two former even believed that a fifth part of the mercury was oxidized, which proportion appears far too great in accordance with my experiments; it is moreover possible, that, in addition to keeping, finer trituration might increase the amount of oxide considerably. Guibourt, on the other hand, arrived at the result that only the one five-hundredth of the mercury was oxidized, that it did not exist in a free state in the ointment, but was combined with an acid. To decide this question, I tested the ætherial solution, which contained the fatty matter of the ointment, by means of a single pair of plates. A strip of sheet copper and of zinc were soldered together at one end in such a manner as to represent in form a tuning fork. When this simple apparatus is immersed in a liquid containing mercury in organic combination, in consequence of the galvanic decomposition the metal is thrown down upon the copper pole in the form of a gray film, which when rubbed upon the copper colours it white. This method has been recommended several times, and is so delicate

* That finely-divided mercury gradually becomes partially converted into oxide is in conformity with Poggendorff's experiments, according to which the surface of a perfectly pure mass of mercury soon loses its mobility for feeble electrical actions. If the mercury be placed in contact with an acid, it reobtains its mobility, which it loses only in gases containing oxygen, not in carbonic acid and hydrogen. See Pogg. Annal., lxxvii. p. 9.

that it detects one-tenth of a grain of corrosive sublimate in an ounce of a solution of albumen. But no mercury could be separated from the blue ointment by this means.

We must therefore undoubtedly consider the oxide as the active ingredient of the blue ointment. But even the oxide cannot be taken into the body without the aid of a solvent; and this solvent is, in all probability, the free acid of the cutaneous secretion. Both the perspiration and the fatty secretion of the sebaceous follicles exhibit an acid reaction; and, according to Anselmino, the perspiration contains a considerable amount of free acetic acid. The acetic acid dissolves the oxide, and this solution readily transudes through animal membranes and the cells of the epidermis.

If this explanation be true, *the greater part of the mercury contained in the blue ointment is perfectly inactive*, and we ought to be able to form a far more active ointment from the pure protoxide. This can, in fact, be done. An ointment containing ʒj. of the black oxide of mercury to ʒij. of fatty matter, hence as much as the blue ointment contains of metallic mercury, acts as an active poison to animals upon which it is rubbed in, and a scruple of it killed a cat in four days, and a rabbit in twenty-four hours. From some experiments which I made upon some patients with an ointment containing only 1 gr. of the oxide to ʒj. of fatty matter, I should consider this preparation as about equal in strength and action to the blue mercurial ointment.

The result which we have obtained in regard to the blue ointment may also be extended to a series of other preparations which are made by the trituration of metallic mercury with various substances, but are destined for internal administration. Among these are the *Æthiops per se*, the *Hyd. c. Cret.* (P. L.), the *Hyd. c. Magn.* (P. Dubl.), the *Æthiops graphiticus* (P. Sax.), *Mercurius gummosus Plenckii*, *Æthiops saccharatus*, *Æthiops tartarisatus Sellii*, *Pil. Hydrargyr.* (P. L.). As metallic mercury is no more able to penetrate the mucous membrane of the intestines than the skin, the action of these preparations can only depend upon the oxide they contain, which is formed by the trituration, and is dissolved by the free acid of the gastric and intestinal secretions. This view was confirmed by a preparation which had been made by triturating 1 part of mercury with 2 of sugar for several hours. When treated with water acidified with sulphuric acid, it yielded a solution which gave a brown turbidity with sulphuretted hydrogen. Most of these preparations have become obsolete on account of their uncertain and feeble action. Moreover, there can be no doubt that the very uncertain action of mercurial ointment does not depend merely upon the various susceptibilities of individuals, but also upon the varying quantity of oxide contained in it; and as individuality always remains an incalculable quantity x, it would be advisable, with a view to obtain the most uniform effects, to substitute for the second x a constant magnitude, and to replace the blue ointment by an ointment containing the protoxide.

II. The poisonous action of the vapour of mercury is well known.

Small animals die in an atmosphere of it; and man, when constantly exposed to its influence by his calling, suffers sometimes from cough and bronchitic symptoms, sometimes from the peculiar mercurial tremors, sometimes from gingival affections, and other phænomena of mercurial cachexy. Although cases of the first kind are attributable to mere local irritation of the respiratory organs, the latter decidedly indicate absorption; hence arises the question, Can the vapour of mercury permeate animal membranes?

It is well known that a piece of gold suspended over a vessel containing mercury soon becomes white, in consequence of the evaporation of the latter. If a thin animal membrane be inserted between the two, the amalgamation ought to continue if the membrane allowed the vapours of the mercury to permeate it. A glass vessel containing mercury was tied over with a piece of peritoneum, the external surface of the latter coated with leaf-gold, and the whole placed in a warm place. In three weeks the gold had not become amalgamated, nor did it become so when the mercury was heated to ebullition, and the internal surface of the peritoneal membrane was coated with globules of mercury.

This experiment shows, *that mercury does not penetrate animal membranes even in the gaseous state; hence it cannot be taken up in the living body.* Some experiments made upon rabbits render it probable that the vapour of mercury, when inspired, condenses within the organs of respiration, there becoming oxidated by intimate contact with the air and gradually absorbed.

1. A rabbit was exposed in a capacious box during an hour to the vapour of boiling mercury. When it was taken out, it crawled with difficulty, and its breathing was very quick, but in the course of the day it recovered itself. The next morning it appeared to be in a very great state of uneasiness. It was again exposed to the vapour of mercury for an hour and a half. Soon afterwards it was seized with tetanic spasms, and died at the third seizure. On dissection, the mucous membrane of the trachea and bronchi was found strongly injected, and the bronchial mucus contained globules of mercury. In the lungs, numerous spots of hyperæmia were found; they varied in size from that of a lentil to a pin's head; also several larger red and gray spots, between which the substance of the lung was in a state of hepatization. By the aid of a lens and the microscope, the nuclei of several of these hyperæmic and hepatized portions were seen to be formed by globules of mercury. This experiment, when repeated several times, always gave the same result.

2. A rabbit was exposed for half an hour to the vapour of mercury. In the course of the day it seemed very dull, did not eat, breathed quickly, and was in a constant tremble; on the following day it was active, and remained so until the fourth day, when it was killed. The bronchial mucous membrane was unchanged; the lungs contained numerous white spots, resembling miliary tubercles, partly surrounded by a hyperæmic line. The microscope detected in the spots granulated cells resembling pus-corpuscles, but no glo-

bules of mercury. The other organs were altered as in the preceding experiment.

3. A rabbit was enclosed in a capacious cage, in which a porcelain trough, 1 foot long and 9 inches in breadth, full of mercury, was placed. The temperature of the room was nearly 39° Fahrenheit. During the first fourteen days no change was perceptible; it then however lost its liveliness, sat in a crouching position, and lost its appetite. It gradually became constantly duller and the respiration quicker; on the twentieth day it dragged its hind legs along; it had a diarrhœa of blackish-brown matter, and on the twenty-second day it was dead. The blood was found loosely coagulated, the stomach and intestines were greatly distended, and the large intestine contained black liquid fæcal matter. The substance of the lung was everywhere compact, and studded with small white spots resembling miliary tubercles and isolated sugillations of the size of a lentil. No globules of mercury could be found.

These experiments prove that the vapour of mercury condenses upon the mucous membrane of the air-passages and in the air-cells of the lungs to globules, there causing inflammation and lobular hepatization; that the mercury subsequently disappears from here; and that after the long-continued action of the vapours of mercury, the phænomena of mercurialization are developed. The experiments have certainly not shown the manner in which the solution and absorption of the globules of mercury takes place. We can only assert thus much, that this cannot possibly occur without previous oxidation.

The results to which the preceding experiments have led may be summed up as follows:—

1. Metallic mercury is not capable of permeating animal membranes either in the finely-divided or gaseous state.

2. On triturating mercury with various substances, a small quantity of protoxide of mercury is formed, and this is the sole active constituent of the blue ointment and several other preparations.

3. The action of the blue ointment is uncertain, because the quantity of oxide contained in it varies according to its age and the mode of preparation.

4. Hence a more uniform and effective preparation can be made from the pure protoxide.

5. Vapours of mercury first produce inflammation of the lungs, subsequently oxidation and absorption take place, and the symptoms of mercurialism commence.—*Journ. für Prakt. Chem.*, No. 9, 1850.

On a new Method of preparing Ethylamine. *By* Dr. A. Strecker.

The beautiful researches of M. Wurtz have made us acquainted with a new class of organic bases, and have thrown much light upon the constitution of the alkaloids in general. Recently M. Hofmann has described a new method of producing these bases by the reaction of ammonia upon the chlorides and bromides of the radicals of

the alcohols. The following method of preparing ethylamine is perhaps more advantageous.

When ordinary æther is made to absorb the vapour of anhydrous sulphuric acid, sulphuric æther properly so called or sulphatic æther ($C^4 H^5 O, SO^3$) is formed, which on the addition of water remains dissolved in the excess of æther, from which it can be separated by spontaneous evaporation.

The sulphatic æther, on treatment with ammonia, behaves like an anhydrous acid; it absorbs this base, forming an ammoniacal salt, which is represented by the formula $4SO^3, C^{16} H^{23} NO^4 + NH^3$. 4 equivs. of the compound æther have absorbed 2 equivs. of ammonia, 1 of which has entered into the composition of the acid. On treating this salt with carbonate of baryta or lead, ammonia is disengaged, and the baryta or lead salt of the new acid, which I have named *ethamic acid*, is obtained. This acid, on treatment with a hot solution of caustic potash, gives off ethylamine, the nature of which was proved by the analysis of the platinum salt, which furnished $C^4 H^7 N, HCl, PtCl^2$. At the same time alcohol and sulphuric acid are formed.—*Comptes Rendus*, August 12, 1850.

On some new Salts of the Organic Alkaloids.

By G. W. Elderhorst.

Hydrofluates.

Hydrofluate of Strychnine.—Strychnine dissolves readily in warm moderately-concentrated hydrofluoric acid. From the solution, concentrated by evaporation, concentrically-grouped prisms, often more than $1\frac{1}{2}$ inch long, separate on cooling, and from which the adherent acid may be removed under a glass over hydrate of lime. It is an acid salt, represented by the formula StrHF+3HF +4HO. It forms colourless four-sided prisms, which are readily soluble in hot water, far less in cold, but somewhat more in hot alcohol. It is insoluble in æther. Its solution has an acid reaction. When heated, it parts with water, then turns red and is destroyed. Over sulphuric acid it loses 3 atoms of water, the crystals become opake, and soften so that they adhere together. At 212° the fourth atom of water is expelled.

Adopting the new equivalents of Nicholson and Abel for strychnine and that of Louyet for fluorine, these results correspond with the formula StrHF+3HF+HO for the salt dried over sulphuric acid, for we have—

Carbon.....	58·96	59·26	59·77	42 =	59·61
Hydrogen.....	6·13	6·18	..	27	6·33
Nitrogen	..	..	..	2	6·61
Oxygen.....	..	..	..	5	9·50
Fluorine	..	..	..	4	17·95

0·863 grm. of the salt dried over sulphuric acid was dissolved in water, mixed with muriatic acid and chloride of platinum, evaporated to dryness on the water-bath in a platinum dish, the residue

macerated with alcohol, and the platinum double salt dried at 212° upon a weighed filter. Its weight amounted to 1·105 grm., corresponding to 79·14 per cent. of strychnine in the hydrofluate; the formula requires 78·98.

0·376 strychnine, dried at 212°, were dissolved in hydrofluoric acid, the solution slowly and cautiously evaporated to dryness, and the mass dried at 212° until it lost no further in weight. The increase in weight amounted to 0·090 grm., corresponding to 23·94 per cent.; the formula requires 23·92.

0·6392 of the air-dried salt lost at 212° 0·0475, corresponding to 7·43 per cent. of water; the formula with 4 atoms of water requires 7·99. 0·324 of the salt, dried over sulphuric acid, lost at 212° 0·005 water, corresponding to 1·5° per cent. The air-dried salt lost consequently over sulphuric acid 7·43−1·53=5·90 per cent. water; 3 atoms make 5·99.

The salt experiences no further loss in weight from 212° to 302°; at a higher temperature it is decomposed. A direct determination of the amount of fluorine by precipitation with chloride of calcium did not furnish a result according with the above determinations.

Strychnine dissolves quite as easily and in large quantity in fluosilicic acid; but only hydrofluate of strychnine is formed, silica being separated.

Hydrofluate of Brucine.—From a solution of brucine in moderately-strong hot hydrofluoric acid, this salt separates on cooling in small, colourless, well-developed prisms, which belong to the trimetric system. It is pretty readily soluble in water, but only sparingly in boiling and imperceptibly in cold alcohol. At 212° it lost 3·34 per cent. of water.

Hydrofluate of Quinine.—Recently-precipitated quinine dissolves plentifully in hydrofluoric acid; but even after great concentration and long standing, the salt does not crystallize. When evaporated nearly to dryness, it is converted into a mass consisting of very slender concentrically-grouped needles, which soon deliquesces in the air. The salt is very soluble in alcohol.

Hydrofluate of Cinchonine.—Recently-precipitated cinchonine dissolves in large quantity in dilute hydrofluoric acid. From the concentrated solution the salt crystallizes in colourless prisms. From alcohol it crystallizes only when the solution is evaporated nearly to dryness in exceedingly-slender concentrically-grouped needles, and then only at the surface, for the subjacent mass is a tenacious yellowish syrup. It is obtained in very beautiful crystals (four-sided prisms, belonging to the trimetric system) from dilute alcohol. At 212° they become milk-white. When heated, the salt turns purple-red, gives a red sublimate, disengages hydrofluoric acid and carbonizes. The air-dried salt gave 2·74–2·88 per cent. water.

0·9358 of the salt, dried at 212°, dissolved in dilute muriatic acid, mixed with chloride of platinum, evaporated to dryness on the water-bath, the residue macerated with a mixture of alcohol and æther, the double salt collected upon a filter, washed and burnt, gave 0·524 grm. platinum, corresponding to 87·52 per cent. According

to the formula CinHF, the salt should contain 88·51 per cent. of cinchonine.

Hydrofluate of Morphine forms colourless four-sided prisms an inch and more in length. It is not very readily soluble in water, and is quite insoluble in alcohol and æther.

Chromates.

Chromate of Cinchonine is obtained in the form of a yellow amorphous precipitate adhering to the glass, on mixing a cold solution of sulphate of cinchonine with a cold solution of bichromate of potash. After a long interval, some yellow prismatic crystals also separate. On employing hot solutions, the precipitate melts to a yellowish-brown very tenacious and viscous mass, which has a satiny lustre when drawn out into threads; on attempting to dissolve these in hot water, they become still darker. Hot alcohol produces the same decomposition.

[To be continued.]

On the Red Colouring Matters of Madder.

By J. Wolff *and* Dr. A. Strecker.

The following are the results obtained by the authors in their investigation:—

Madder contains two red colouring substances, which have long been known by the names of *alizarine* and *purpurine*, given them by MM. Robiquet and Colin. The same substances were described by M. Runge under the names of *Krapproth* and *Krapppurpur*; M. Debus has called them *lizaric* and *oxylizaric* acids.

The composition of alizarine is represented by the formula $C^{20} H^6 O^6$, which exactly corresponds with the results of the analyses of Mr. Schunck and M. Debus. Alizarine is a weak acid which unites with bases in different proportions. The authors have analysed and calculated the following salts:—

Hydrated alizarine	$C^{20} H^6 O^6 + 4HO$
Alizarine with lead	$2(C^{20} H^5 O^5) + 3PbO$
Ditto another preparation	$3(C^{20} H^5 O^5) + 4PbO$
Alizarine with lime	$2(C^{20} H^6 O^6) + 3(CaO, HO)$
Alizarine with baryta	$C^{20} H^6 O^6 + 2BaO$
Ditto another preparation	$2(C^{20} H^6 O^6) + 3(BaO, HO)$
Ditto dried at 248° F.	$2(C^{20} H^6 O^6) + 3BaO$
Ditto another preparation	$3(C^{20} H^6 O^6) + 2BaO.$

The chloronaphthalic acid, $C^{20} H^5 ClO^6$, discovered by M. Laurent, is chlorinated alizarine, as evident from the above formula for alizarine. This acid forms with oxides salts of a red or yellow colour. It was in vain attempted to convert the acid into alizarine either by potassium amalgam or by an electrical current passed through an alkaline solution; it is however highly probable that subsequent investigations will lead to a reaction which theory presents as possible.

Alizarine furnishes with nitric acid oxalic acid and a volatile acid

which Mr. Schunck calls *alizaric acid*, and which was recognised to be phtalic acid by MM. Gerhardt and Laurent. The authors have confirmed this statement by the analysis of the silver salt, which furnished $C^{16} H^4 Ag^2 O^8$. The following equation explains this metamorphosis :—

$$\underset{\text{Alizarine.}}{C^{20} H^6 O^6} + O^8 + 2HO = \underset{\text{Phtalic acid.}}{C^{16} H^{16} O^8} + \underset{\text{Oxalic acid.}}{C^4 H^2 O^8}.$$

M. Laurent found that chloronaphtalic acid is likewise converted, under the influence of nitric acid, into phtalic and oxalic acids, another proof of the intimate connexion existing between this acid and alizarine.

Purpurine, the second red colouring substance of madder, is represented by the formula $C^{18} H^6 O^6$; it differs from alizarine by 2 equivs. of carbon. It furnishes, like alizarine, all the colours which are produced by madder with the different mordants. The Adrianople red produced with purpurine is far more beautiful (less blue) than that obtained with alizarine. Purpurine is separated from alizarine by a concentrated boiling solution of alum, in which it dissolves very readily. It furnishes a currant-red solution with potash, whilst the colour of the potash solution of alizarine is a pure blue by reflected light, and purple when placed between the eye and the light.

Purpurine is likewise converted into phtalic and oxalic acids by nitric acid according to the equation—

$$\underset{\text{Purpurine.}}{C^{18} H^6 O^6} + HO + O^5 = \underset{\text{Phtalic acid.}}{C^{16} H^6 O^8} + \underset{\text{Oxalic acid.}}{C^2 HO^4}.$$

In madder which had been fermented by the addition of yeast at a temperature of 86° F., only purpurine could be detected; it is very probable that the alizarine is converted under these circumstances into purpurine, which might occur with evolution of carbonic acid and hydrogen.—*Comptes Rendus*, August 12, 1850.

ANALYTICAL CHEMISTRY.

On a new Method for the Determination of Iron in Clay-band and Black-band Ironstone. By Dr. Frederick Penny, *Professor of Chemistry in the Andersonian University, Glasgow**.

In the course of certain investigations which I had occasion recently to undertake upon the materials and products of the manufacture of alum from "alum-shale," I was very much retarded by the want of a ready process for the quantitative determination of the protoxide and peroxide of iron. There are various well-known analytical methods in use among chemists for the estimation of iron. Several of these methods give very accurate results, and when the

* Communicated by the Author, having been read at the Meeting of the British Association in Edinburgh, 1850.

compound of iron to be analysed is unmixed with foreign matters, the necessary operations are easily performed; but when, as is usually the case, the compound of iron occurs mixed with other substances, and especially with alumina and phosphates, the exact determination of its amount by any one of the ordinary processes is both tedious and difficult, requiring considerable time and a certain degree of practical skill on the part of the operator. When the two oxides are associated together, the problem becomes still more complex; and in those cases where comparatively large quantities of material have to be examined, the common methods of analysis are scarcely available. At any rate, I found them to be altogether unsuitable for the experiments alluded to; and I was therefore compelled to search for a more convenient and more expeditious method of procedure.

It is not necessary for the object of the present paper to give a detailed account of the many trials I made to discover a process adapted for the purpose I had then in view. Suffice it to say, that after various unsuccessful experiments, and repeating Marguerite's process with the permanganate of potash (prepared according to Dr. Gregory's method), I was induced to try the neutral chromate of potash, and was speedily convinced that it might be most advantageously employed for the estimation of the oxides of iron. After carefully studying the phænomena of its action, and the best mode of applying it, I used it extensively in the investigations before referred to.

I have since extended the application of this salt to the analysis of the common ores of iron, especially the clay-band and black-band ironstone of this country, and I have also employed the bichromate of potash for the same purpose. Both these salts, when used with certain precautions, give very exact results; and they possess the advantage, that a much larger quantity of the ore may be operated upon than can be conveniently treated by the usual methods. The process requires no other apparatus than that commonly used for centigrade testing, which is familiar to most persons engaged in chemical pursuits. It may be easily and rapidly executed, occupying only a fraction of the time required for the process of estimating iron by precipitation as the sesquioxide, and may be performed by any one moderately skilled in chemical manipulations. For these reasons, as well as from the great service it has been to myself, I am induced to think it is likely to prove serviceable to practical men; and I have been led to offer an account of it to the British Association, in the hope that it may become generally known and applied.

It will be at once obvious to those conversant with the chemical relations of the chromates, that the process is based on the well-known reciprocal action of chromic acid and protoxide of iron, whereby a transference of oxygen takes place, the protoxide of iron becoming converted into the sesquioxide, and the chromic acid into sesquioxide of chromium. The following equation will serve to exhibit the nature of this reaction:—

$$2CrO^3 + 6FeO = Cr^2O^3 + 3Fe^2O^3.$$

Now, in clay-band and black-band ironstone the iron exists chiefly in the state of a carbonate of the protoxide. When therefore the ore is boiled in hydrochloric acid, the iron is converted into the protochloride; and on adding bichromate or neutral chromate of potash to the solution, the chromic acid will be deoxidized, and the protochloride of iron will become the sesquichloride. These changes may be thus explained:—

$$KO, 2CrO^3 + 6FeCl + 7HCl = 3(Fe^2\,Cl^3) + Cr^2\,Cl^3 + KCl + 7HO.$$

The quantity of chromic acid decomposed, and consequently of either chromate consumed, must obviously be exactly proportionate to the amount of protochloride of iron existing in the solution. If therefore we can ascertain with certainty the precise moment when the protochloride of iron is completely converted into perchloride, we can easily determine the quantity of chromate required, and thence deduce the proportion of iron in the ore. This desideratum is fully supplied by the red prussiate of potash (ferridcyanide of iron), which has long been patent as one of the most delicate tests for the detection of protosalts of iron. It gives with these, even when largely diluted with water, a rich blue precipitate of prussian blue, while with dilute solutions of the ordinary persalts of iron it produces a greenish or reddish tinge. Its delicacy in indicating the presence of a protocompound of iron is such, that a weak solution of it will cause a distinct coloration, when added to a *drop* of a solution of protosulphate of iron, containing 1 part of the sulphate to 10,000 parts of water; and if it be applied to a considerable quantity of the ferruginous solution, a far more minute proportion can be discovered.

In order therefore to decide when a sufficient quantity of the chromate has been added, we have only to test occasionally a small portion of the iron solution with a dilute solution of the red prussiate of potash. So long as a trace of protochloride of iron remains unchanged, a blue colour will be produced; when the action approaches towards completion, a greenish shade will be communicated, and this will very soon be followed by a reddish tinge, which indicates that the operation is finished.

I have already mentioned, that both the chromate and the bichromate of potash may be used for estimating the amount of iron in the common ores of this metal. The action of both salts is in every respect similar.

When rigorous and minute results are required, the chromate is certainly to be preferred. It is more extensively soluble in water, and a larger proportionate quantity of it is necessary to produce the same amount of effect. But for practical purposes, the bichromate will undoubtedly be found the more convenient; it can be more readily purchased, and may be easily purified by crystallization. In the present paper therefore I shall purposely confine my observations to the employment of the bichromate. I may remark, that this salt has already been incidentally recommended for estimating the quantity of sulphate of iron employed in a particular

process, for testing the value of commercial peroxide of manganese, but it has never been applied, so far as I am aware, to the analysis of ironstone.

Before describing the details of the mode of applying this salt to the analysis of the ores of iron, I must briefly mention the results of certain experiments which I made for the purpose of testing the accuracy of the present process, and of rigorously ascertaining the exact proportion of the bichro nate corresponding to a certain quantity of iron. At first I was inclined to calculate the ratio of these substances from their equivalent numbers; but on reference to the results which have been given by different experimenters for the determination of the equivalent of chromium*, I found such wide discrepancies, that it became necessary to ascertain the proportion by actual experiment.

In the first series of experiments, pure harpsichord wire was dissolved with every care in hydrochloric acid, and bichromate of potash added to the solution until the conversion of the protochloride of iron into the perchloride was complete. I obtained the following results:—

		Iron.		Bichromate.
Exp.	I.	50 grains	required	44·4 grains.
...	II.	39·7	...	35·2 ...
...	III.	48·3	...	42·8 ...
...	IV.	55·3	...	49·2 ...

The mean of these results is, 100 parts of iron to 88·75 of bichromate.

In the second series of experiments, protosulphate of iron was employed. This salt was made from protosulphuret of iron, and purified most carefully by repeated crystallization. A known quantity of it was dissolved in water, acidulated with either pure hydrochloric or sulphuric acid, and the solution treated with bichromate:—

		Sulphate of iron.		Bichromate.
Exp.	I.	100 grains	required	17·90 grains.
...	II.	180	...	32·10 ...
...	III.	150	..	26·82 ...
...	IV.	120	...	21·40 ...

These experiments give the ratio of 100 parts of sulphate of iron to 17·867 of bichromate, or 100 of iron to 88·71, which corresponds very closely to the mean result obtained with the metallic iron. Moreover, I performed a series of similar experiments with the neutral

* The following are some of the equivalents which have been assigned to chromium on the hydrogen scale:—

Berzelius	27·906
Turner	28·08
Berlin	26·27
Peligot	26·24
Kane	28·14
Jacquelain	25·04
Moberg	26·79
Lefort	26·68

chromate of potash, and obtained results completely confirmatory of the general accuracy of the foregoing experiments. We may, therefore, I think, safely conclude, that 100 parts of metallic iron correspond to 88·75 of the bichromate of potash, and that 100 of the latter are equal to 112·67 of the former. I may remark, that these results give very nearly 27 for the equivalent of chromium; though I do not for a moment pretend that the present experiments have that rigorous exactness which is essential for the determination of an atomic weight.

I shall now proceed to describe the method of employing the bichromate of potash for the determination of the amount of iron in clay-band and black-band ironstone. I shall be purposely minute, as I particularly desire that the process may be serviceable to those who, from their pursuits in life, are interested in the value and quality of ironstone, and who may be imperfectly acquainted with analytical operations.

A convenient quantity of the specimen is reduced to coarse powder, and one-half at least of this still further pulverized, until it is no longer gritty, between the fingers. The test solution of bichromate of potash is next prepared. 44·4 grs. of the salt in fine powder are weighed out, and put into an alkalimeter (graduated into 100 equal divisions), and tepid distilled water afterwards poured in until the instrument is filled to 0. The palm of the hand is then securely placed on the top, and the contents agitated by repeatedly inverting the instrument, until the salt is dissolved and the solution rendered of uniform density throughout. It is obvious that each division of the solution thus prepared contains 0·444 gr. of bichromate, which corresponds to $\frac{1}{2}$ a grain of metallic iron. The bichromate of potash used for this process must of course be purchased pure, or made so by repeated crystallization, and it should be thoroughly dried by being heated to incipient fusion.

100 grs. of the pulverized ironstone are now introduced into a florence flask, with $1\frac{1}{2}$ oz. by measure of strong hydrochloric acid, and $\frac{1}{2}$ an ounce of distilled water. Heat is cautiously applied, and the mixture occasionally agitated, until the effervescence caused by the escape of the carbonic acid ceases; the heat is then increased and the mixture made to boil, and kept at moderate ebullition for ten minutes or a quarter of an hour. During these operations it will be advisable to incline the flask, in order to avoid the projection, and consequent loss, of any portion of the liquid by spirting. About 6 oz. of water are next added, and mixed with the contents of the flask, and the whole rapidly transferred to an evaporating basin. The flask is rinsed several times with water, to remove all adhering solution.

Several small portions of a weak solution of pure red prussiate of potash (containing 1 part of the salt to 40 of water) are now dropped upon a white porcelain slab, which is conveniently placed for testing the solution in the basin during the next operation.

The prepared solution of bichromate of potash in the alkalimeter is then added very cautiously to the solution of iron, which must be

repeatedly stirred, and as soon as it assumes a dark greenish shade, it should be occasionally tested with the red prussiate of potash. This may be easily done by taking out a small quantity on the end of a glass rod, and mixing it with a drop of the solution on the porcelain slab. When it is noticed that the last drop communicates a distinct red tinge, the operation is terminated. The alkalimeter is allowed to drain for a few minutes, and the number of divisions of the test liquor consumed read off. This number multiplied by two gives the amount of iron per cent. in the specimen of ironstone, assuming that, as directed, 100 grs. have been used for the experiment. The necessary calculation for ascertaining the corresponding quantity of protoxide is obvious.

When black-band ironstone is the subject of analysis, or when the ore affords indications, by its appearance or during the treatment with hydrochloric acid, that it contains an appreciable quantity of carbonaceous matter, then the hydrochloric acid solution must be filtered before being transferred to the basin, and the filter with the insoluble ingredients must be washed in the usual way with warm distilled water, slightly acidulated with hydrochloric acid, until the filtrate ceases to give a blue colour with red prussiate of potash. In those cases also where the presence of iron pyrites in the ironstone is suspected, it will be necessary to remove the insoluble matter by filtering before applying the bichromate solution; but with ironstones in which the insoluble ingredients are merely clay and silica, filtration is not essential.

Now it is evident that the foregoing process, so far as I have described it, serves for the determination of that portion of iron only which exists in the ore in the state of protoxide. But many specimens of the common ironstone of this country contain appreciable quantities of peroxide of iron, which, being unacted upon by the bichromate of potash, would escape estimation by the present method. By an additional and easy operation, however, the amount of metallic iron in this ingredient may be likewise determined. It is only necessary to reduce it to the minimum state of oxidation, and then to add the bichromate as previously directed.

The best and most convenient agent for effecting the reduction of the persalts of iron is sulphite of soda. The only precaution to be observed is to use it in sufficient quantity, and at the same time to take care that the iron solution contains excess of acid. When the reduction is complete, a few minutes' ebullition suffices to decompose the excess of sulphite of soda, and effectually to expel every trace of sulphurous acid.

In order to test the exactness of this mode of estimating the iron in the peroxide, I made several experiments with peroxide prepared from known quantities of pure iron wire. The peroxide was thoroughly washed, dissolved in hydrochloric acid, reduced with sulphite of soda, and after complete expulsion of the excess of sulphurous acid, the solution was diluted with water and treated with bichromate of potash. I select three of the experiments:—

Exp.	I.	10 grains of iron consumed		8·87	of bichromate.
...	II.	18	...	15·94	...
...	III.	25	...	22·15	...

The mean of all my experiments on this point gives the ratio of 100 of iron to 88·6 of bichromate, which is in close accordance with the former results.

Whenever therefore the ore of iron contains peroxide, it will be necessary to add sulphite of soda to the hydrochloric acid solution, before the addition of the test-liquor from the alkalimeter. The sulphite should be dissolved in distilled water, and added to the solution of iron in small successive portions, until a drop of the liquor gives merely a rose-pink colour with sulphocyanide of potassium, which indicates that the reduction of the persalt of iron is sufficiently perfect. The liquid is now heated till the odour of sulphurous acid is no longer perceptible. These operations should be performed while the solution is in the flask, and before it is filtered or transferred to the basin.

I will here mention, for the guidance of those who may not be fully aware of the reactions of the oxides of iron, that the existence of an appreciable quantity of peroxide in the ironstone may be readily discovered by dissolving (as directed in the process) 30 or 40 grs. of the ore in hydrochloric acid, diluting with about 8 oz. of water, filtering and testing a portion of the solution with sulphocyanide of potassium. If a decided dark blood-red colour is produced, the quantity of peroxide in the stone must be determined; but if the colour is only light red or rose-pink, the proportion is exceedingly small, and for practical purposes not worth estimating. Of course, when the specimen of ironstone has an ochrey or a reddish appearance on the surface or in the fracture, the presence of a large proportion of peroxide is indicated, and its exact quantity must be determined.

In conclusion, I must not omit to notice one or two circumstances which appear at first to militate against the accuracy of this process. It may be questioned whether solutions of the protosalts of iron do not absorb oxygen so rapidly from the air as to influence the results obtained by this method. Marguerite has shown, and my own observations completely confirm his statement, that protosalts of iron, in an acid solution, become peroxidized very slowly; and, in a particular experiment, I found that contact with the air during several hours caused no diminution in the quantity of bichromate of potash required. As the process may be completed in a few minutes, it is certain that no inaccuracy can arise from this cause.

It is also important to inquire, whether the chromic acid in the chromates of potash may not be partially deoxidized by hydrochloric acid alone without the presence of a protosalt of iron. Such a reaction would obviously give rise to a serious error. It is well known that concentrated hydrochloric acid rapidly decomposes the chromic acid of the chromates when aided by the application of heat. But I have satisfied myself by numerous experiments, that this acid

exerts very little appreciable action upon dilute solutions of the chromates of potash, either cold or warm, and that the action is only partial even after continued ebullition; so that the present method is free from inaccuracy on this account.

The present paper might be much extended, by showing the applications of this mode of estimating iron and its oxides to the analysis of other ores of the same metal, as well as its availability for the examination of alum liquors and copperas liquors, and other products in the arts. But this would be departing from the object I have in view; and such applications can easily be made by any one ordinarily acquainted with practical chemistry.

I have also employed the bichromate of potash for the analysis of crystallized protochloride of tin, and with very great advantage for the estimation of nitric acid. I reserve the description of these applications for a future communication.

I may take this opportunity of making a single remark with reference to Marguerite's new method for estimating iron. I have made extensive trials of it at different times, and I believe it has been much used by other chemists. It is undoubtedly a very elegant, and also a delicate process, and for any particular set of experiments it leaves little to be desired; but I have invariably found that the prepared test solution of permanganate of potash undergoes spontaneous decomposition and deterioration by keeping, so that it becomes necessary to test its strength before almost every series of experiments, or frequently when it requires to be kept ready for daily use. This I consider to be a serious disadvantage as regards its general application, and one which will much interfere with its usefulness to practical men.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Edinburgh, July 31*st,* 1850.

The following are abstracts of the principal communications brought before the Chemical Section, as reported in the *Athenæum*:—

On the Per-centage of Nitrogen as an Index to the Nutritive Value of Food. By Dr. A. Voelcker.

The object of this paper was to show that the usual estimation of the nutritive qualities of an article of food is frequently attended with inaccuracies, which renders it desirable to modify our present methods in this respect in many cases. A circumstance which leads to considerable error is, the presence of ammoniacal salts in the juices of plants. In order to prove experimentally the presence of ammoniacal salts in larger quantities than hitherto suspected, and to

avoid the objection that they might result from a partial decomposition of albuminous substances during the analysis, the author chose fungi for his experiments, which are rich in nitrogen and known as being highly nutritious. The species used was *Agaricus prunellus*, a species which is edible, and remarkable for forming most beautiful fairy rings. After having separated all soluble proteine compounds by means of basic acetate of lead, which reagent throws down these completely, the amount of nitrogen still present in the juice of these agarics, in the form of ammoniacal salts, was found to be 0·204 per cent. for the fresh fungi, or 1·82 per cent. for the dry fungi. The whole amount of nitrogen in the same agarics, collected at the same time, determined by combustion, was found to be 0·74 per cent. for the fresh fungi, or 6·61 per cent. for the fungi dried at 212° F. Deducting from the last-stated numbers the quantity of nitrogen found to exist in the juice in the form of ammonia, we find that only 0·536 per cent. of nitrogen in the fresh, or 4·799 per cent. of nitrogen in the dry fungi, exists in the state of proteine compounds, and that nearly one-third of the nitrogen obtained by direct combustion exists in the form of ammonia in the juice, or at all events in a form in which the nitrogen adds nothing to the nutritive value of the fungi. The nutritive value of fungi has thus been overrated considerably; and there can be little doubt that the same is the case with many vegetables, which according to the author's experiments contain sometimes considerable quantities of ammonia in the form of ammoniacal salts.

Dr. Christison remarked that he had long been convinced that there was a considerable fallacy in the methods of determining the value of food, and he hoped Dr. Voelcker's communication would direct inquiry in a more satisfactory direction.

On a peculiar Form produced in a Diamond when under the influence of the Voltaic Arc. By J. P. Gassiot.

M. Jacquelain was the first to show, that when the diamond is submitted to the high temperature and influence of the voltaic arc, it quickly becomes converted into a black carbonaceous matter having all the appearance of coke. The diamond when in a native state is an insulator or non-conductor of electricity, but when thus changed into coke it becomes an excellent conductor. At the Chemical Section of the British Association, held at Oxford in 1847, Dr. Faraday exhibited some specimens of the diamond coke which had been forwarded to him by M. Jacquelain, and subsequently, on the 16th of June 1848, he publicly showed the experiment in London, in the theatre of the Royal Institution. On repeating the experiment a short time since before a few private friends, I obtained a product so totally different from that of M. Jacquelain, that I am induced to bring the subject before this Section, in the anticipation that it may tend to elicit some observations on a phænomenon which at the time attracted the attention of many electricians. The apparatus I used in the experiment consisted of forty series of the usual

size of Grove's nitric acid battery; the terminals were made from two pieces of well-burnt box-wood charcoal, that attached to the positive or platinum end of the battery being formed in the shape of a small cup or crucible, in which the diamond was placed; to the negative or zinc end of the battery a piece of the same charcoal (but *pointed*) was attached. The experiment was then made in the same form as described by M. Jacquelain, by first making contact with the two charcoal terminals, then bringing the flame in such a position as to cause it to *surround* the diamond; in less than one minute the diamond as well as the electrode became in a state of intense ignition. The diamond gradually increased in size, rolling about in the heated crucible; when it suddenly expanded, forcing itself upwards on the negative terminal, at which moment I separated the electrodes. The diamond, which was in a state of intense ignition, remained attached to the negative terminal. When cool it exhibited the same state as it now presents. It was expanded to eight or ten times its original bulk. Instead of becoming a black carbonaceous substance and a good conductor, it has a vitreous, white, opake appearance, and remains a non-conductor. It has also a deep circular cavity on that portion which was opposite and nearest to the positive electrode; that part which was in contact with the negative electrode being clearly discernible by a small portion of the box-wood charcoal remaining attached to it. The centre of the cavity appears to be still brilliant, as if that portion of the diamond had not been in a complete state of fusion. In one or two other experiments the diamonds disintegrated, the fragments remaining in a carbonaceous state; since which I have not had the opportunity of repeating the experiment.

On some Amalgams. *By* J. P. Joule.

The author had procured an amalgam of iron by precipitating it on mercury by the electrotype process. He had subsequently pursued the research with a view to form definite amalgams by a simple chemical or mechanical process. When mercury was made negative under a solution of sulphate of copper, an amalgam of copper was formed, which, when fully saturated with copper, was found to be represented by the formula $Cu + Hg$. The author also exhibited a small apparatus whereby amalgams could be made to endure a pressure of 60 tons per square inch of surface. The superfluous mercury was thus expelled through the openings in the sides of the press, leaving an amalgam of definite chemical composition. In this way he had procured the following compounds:—

$$\begin{aligned} Pt &+ 2Hg \\ Ag &+ 2Hg \\ Cu &+ Hg \\ Fe &+ Hg \\ 2Zn &+ Hg \\ 2Pb &+ Hg \\ 7Sn &+ Hg \end{aligned}$$

On the Sugar Produce of the South of Spain, chiefly in connexion with the employment of the Acetate of Lead and Sulphurous Acid as purifying agents. *By* Dr. SCOFFERN.

On the southern coast of Spain, in a region limited by Almeria on the east and Malaga on the west, bounded on the north by mountain ranges and on the south by the Mediterranean, is a tract of land which, so far as its climate and productions are concerned, may be aptly denominated tropical. In it the date, palm, indigo, cotton and sugar-cane flourish with vigour, yielding products equal both in quantity and quality to those of the tropics themselves. The sugar-cane, first introduced by the Arab conquerors, is not only consumed in large quantities as a dessert, but also gives rise to a considerable manufacture of raw and refined sugar, a circumstance which beyond Spain itself seems to be very little known.

There is perhaps no example on record of any operation involving a commercial result attended with such an enormous destruction of material as the operation of extracting sugar from the cane. One portion of this loss is due to mechanical, another to chemical causes. The sugar-cane has been stated by most writers who have found opportunities of practically examining the subject to contain no more than 10 per cent. of solid non-saccharine matter, leaving 90 per cent. of juice to be extracted. Of this 90 per cent. most writers concur in testifying that in practice scarcely 50 per cent. are actually obtained, at least in the British West India possessions. Cane-juice itself has usually been stated to contain from 17 to 23 per cent. of crystalline sugar, of which scarcely 7 per cent. in practice is actually extracted. Considerable doubts having been expressed as to these statements of the amount of juice in the cane, and sugar in the juice, I have lately gone through a series of experiments having for their object the settlement of the doubt, and with the result of amply confirming the testimony of other experimenters. Having operated on canes from various parts of this district by slicing them, exhausting first by hot water and then by hot alcohol, and finally drying, I obtained as my mean result about 10 per cent. of woody or insoluble matter, whilst the sugar extracted and crystallized ranged from 17 to 23 per cent., as had previously been stated. It would consequently appear that 40 per cent. of juice is actually lost in the practice of our West India workings; and now arises, as a most important consideration, the question as to what extent this loss is inevitable, and to what extent it might have been obviated by altered machinery or improved manipulation. Instead of 50 per cent. of juice extracted, 70 per cent. is much nearer the average amount yielded by the sugar-mills of this coast, although occasionally the result is as high as 75 per cent., and this in some cases with mills of very inferior construction. The cane however is passed between the rollers of the mill four times, until the refuse or megass, as the pressed cane is called, has been reduced to a state of disaggregation resembling ground tan, whereas the West India cane refuse is represented to be in the form of long strings, a sufficient proof that

the pressure applied has been very inadequate. After the cane has finally left the mill, it is immediately, in the Spanish sugar regions, subjected to the operation of pressing, sometimes by the agency of a screw, but in many cases by hydrostatic force. By the latter method, I have seen 13 per cent. of juice extracted from megass which had already yielded up 73 per cent. of juice to the mill, thus elevating the total quantity extracted to 86 per cent. out of the original 90, and consequently as a manufacturing operation leaving very little more to be desired. The hydrostatic press I consider to be an apparatus which is indispensable to the œconomy of every sugar estate; not only does it largely contribute to the amount of juice extracted, but what is most remarkable, the juice resulting from hydrostatic pressure of megass is invariably, so far as my observations have gone, richer in sugar than juice yielded by the mill, a fact which seems to be only explicable on the supposition, that the hydrostatic press, in virtue of its great power, is enabled to extrude those particles of sugar which microscopic examination demonstrates to exist in the cane in the solid and crystalline form.

The subsequent stages of the sugar manufacture as carried on in Spain do not materially differ from those in operation in Cuba, and many other tropical countries. The juice is defecated or purified by lime, skimmed, evaporated to the requisite degree, and poured into earthenware moulds, the contents of which are finally exposed to the operation of claying. In one manufactory, however, witnessed by me, at Almunecar, lime is no longer used on account of its well-known injurious effects on sugar; no other agent having been substituted in its stead, but sole reliance being placed on the coagulation by heat of albuminous matters present in the juice, and their final removal by skimming. Under this system of manufacture the sugar produced is light coloured, but badly grained, and the unseparated albuminous matters are present in such quantity that every 100 parts of the concentrated saccharine juice as it comes from the teache, or last evaporating pan, only yield 40 parts of crystallized sugar on cooling, the other 60 per cent. remaining in the condition of molasses perfectly uncrystallizable until some adequate means for defecation be had recourse to.

The chief object of my residence in this sugar district was to superintend the erection of machinery for manufacturing sugar by means of my own process. The site of our operations is Montril, about forty-five miles south of Granada, in a manufactory furnished with apparatus of the rudest character. Up to this period (July 9) our own vacuum apparatus has not been sufficiently advanced to enable us to pursue our operations by its aid; nevertheless, owing to the superior defecating power of the subacetate of lead, we have, even with the old and rude machinery, obtained a result of more than 16 instead of 7 per cent. of sugar. Our striking teaches, or final evaporating pans, we were under the necessity of removing in order to afford the requisite space for our own machinery; hence we were reduced to the necessity of concluding our process of concentration in a brass pan of conical form and holding about 600

imperial gallons, thus materially increasing the difficulty of the evaporative process. Hitherto the juice has been mixed with only one-sixth per cent. of the subacetate, but I imagine the quantity may be advantageously increased. As filtration is indispensable for the conduction of this process, considerable fear was entertained lest fermentation might supervene. This fear, however, practice has demonstrated to be groundless, inasmuch as we possess in sulphurous acid an agent most antagonistic to fermentation. Another speculative fear was, lest danger might arise from the lead employed; this fear, too, practice demonstrates to be entirely without foundation(?), for not only is the sulphite of lead most easily removed, but even were it to remain no injury could supervene, inasmuch as this agent is as harmless as chalk.

Dr. Gregory stated, that he had made experiments on the sulphite of lead formed in this process. He admitted that an infinitely small proportion might still remain in the sugar, but that he considered it quite innocuous. He had indeed fed rabbits and dogs with food which had been united with this sulphite of lead, and the result was that they thrived amazingly, showing no symptom of any of the known effects of lead. Dr. Gregory also remarked, that in testing sugar for lead with the hydrosulphate of ammonia, iron was often mistaken for the former metal.

Dr. Christison contended that we had no evidence that the sulphite of lead was innocuous. It was true that in cases of poisoning by carbonate of lead, sulphuric acid was administered to convert it into the comparatively insoluble sulphate; but this was a case widely different from the slow accumulation of lead in the system. Dr. Christison adduced some examples of exceedingly small doses of lead being taken in water for more than twelve months before its evil effects became apparent. He therefore thought it yet remained to be proved that the sulphite of lead was without action on the system, since we know nothing of the influence of the solvents it would meet with in the system, or of the influences of vital action. Rabbits, he was prepared to say, should be entirely rejected in these inquiries, since he had found that they were not affected by many poisons. Dogs and cats were the only animals which could from their internal structure be regarded as the representatives of the human system in these investigations.

Some Observations on the Growth of Plants in Abnormal Atmospheres. *By* Dr. J. H. Gladstone *and* Mr. G. Gladstone.

Whereas oxygen is the most important constituent of the atmosphere so far as animal life is concerned, it is upon the carbonic acid, ammonia and aqueous vapour that the vegetable world is supremely dependent. The question arises, Does the oxygen and nitrogen of the air play no important part in the process of vegetation? The following preliminary experiments, with a view to the solution of this and similar inquiries, were detailed by the authors. A pansy lived for the length of twenty-four days in an atmosphere

of hydrogen containing 5 per cent. of carbonic acid; one similarly placed in an atmosphere of common air remained healthy for a longer period. Five onions just commencing to sprout were severally placed in carbonic acid, carbonic oxide, coal gas, air containing 8 per cent. of light carburetted hydrogen, and ordinary atmospheric air. The germination of the first two was entirely stopped, while the hydrocarbons appeared considerably to accelerate the growth of the vegetable. The plants in each instance lost weight. A pansy in flower, a young stock and a grass plant were placed in pure nitrogen gas. The former two soon died, but the grass was left growing a month after the commencement of the experiment. Another pansy was placed in a mixture of oxygen and hydrogen gases in the proportion requisite to form water. In order to imitate the balance that obtains in nature between animal and vegetable life, some flies were introduced, along with some sugar to serve as their food. The experiment was commenced a fortnight since, and the plant when last observed was in good condition. Owing to the low specific gravity of the mixed gases, the flies were unable to mount on the wing or make the usual buzzing noise; but the substitution of hydrogen for nitrogen in the atmosphere had no marked effect upon their breathing, thus confirming the observations of M. Regnault by an instance drawn from the Articulata.

On the Incrustation which forms in the Boilers of Steam-Engines. In a letter addressed to Dr. G. Wilson, F.R.S.E., *by* Dr. J. Davy.

On entering upon this inquiry, which I did after my return from the West Indies in December 1848, and after communicating a short paper to the Royal Society "On Carbonate of Lime in Sea-Water," it appeared to me desirable to collect as many specimens as possible of incrustation from the boilers of steam-vessels, now so widely employed in home and distant navigation. By application to companies and to friends in our sea-ports, as Dundee, Hull, Southampton, Hayle, Liverpool, Whitehaven, I have succeeded in procuring specimens of incrustation formed by deposition in voyages from port to port in the British and Irish Channels and the North Sea, between Southampton and Gibraltar, in the Mediterranean and the Black Sea, and in the Atlantic Ocean, between Liverpool and North America, and between Southampton and the West Indies. I am promised specimens from the Red Sea and the Indian Ocean, but these I have not yet received.

The character and composition of the incrustation, whether formed from deposition from water of narrow seas or of the ocean, I have found very similar; with few exceptions, crystalline in structure, and, without any exception, composed chiefly of sulphate of lime; so much so indeed that, unless chemically viewed, the other ingredients may be held to be of little moment, rarely amounting to 5 per cent. of the whole. From two specimens of incrustation from the boilers of steamers crossing the Atlantic, one of which you sent me, in which you had detected a notable portion of fluorine, judging

from its etching effect on glass, I also procured it; it was in combination with silica; and procured it also so combined from two obtained from steamers navigating our own seas, one between Dundee and London, the other between Whitehaven and Liverpool. Of this I had proof, by covering with a portion of glass or platina foil a leaden vessel charged with about 200 grs. of the incrustation mixed with sulphuric acid, and by keeping the glass cool by evaporation of water from its surface, and by supplying moisture for the condensation of the silicated gas by a wet band round the mouth of the vessel. After about twenty-four hours under this process, a slight but distinct deposition was found to have taken place, corresponding to the margin of the vessel, a deposition such as that produced by silicated fluoric acid gas under the same circumstances. Thus it was not dissipated by heat nor dissolved by water, and yet admitted of removal by abrasion, either entirely or in great part, the former in the instance of the platina foil, the latter in that of the glass. Besides the ingredients above mentioned, I may add that, in many instances, oxide of iron, the black magnetic oxide, was found to form a part of this incrusting deposit, collected in one or more thin layers; and further, that in some, especially of steamers navigating the narrower and least clear part of the British Channel, the depositions presented a brownish discoloration, produced by the admixture of a small quantity of muddy sediment. Incrustations so discoloured, I may remark, are reported to be most difficult to detach.

I have said that the incrustations, with few exceptions, were similar in their structure, and that that was crystalline; it was not unlike the fibrous variety of gypsum of the mineralogists. The specimens received, as might have been expected, varied very much in thickness, viz. from one line and less to half an inch. I have endeavoured, by a set of queries which I had distributed, to obtain information respecting the exact time in which the incrustations were formed, and under what circumstances; but with partial success only, owing, it may be inferred, to a want of exact observation. In one instance, that of the North American mail ship Europa, which arrived at Liverpool on the 15th of November at 4 P.M., having left Boston on the 7th of the same month at 9 A.M., an incrustation was found in her boiler of about one-fiftieth of an inch in thickness; and it is stated that an incrustation of about the same thickness was found on her outward voyage. This example may aid in giving some idea of the degree of rapidity with which the incrustation is produced, at least in the Atlantic, with the precaution of "blowing off" every three hours, and with the "brine pumps" kept in constant work. In other seas, especially contiguous to shores, and more especially of shores formed by volcanic eruptions, it is probable, *cæteris paribus*, the rate of the deposition of the incrusting sulphate of lime will be more rapid. The results of the trials of several portions of sea-water taken up on the voyage from the West Indies to England noticed in the paper of mine already referred to, are in favour of this conclusion.

To endeavour to prevent the deposition of the incrusting matter or to mitigate the evil, various methods, it would appear, have been had recourse to, some of a chemical kind, as the addition of muriate of ammonia and sulphate of ammonia to the water in the boiler, without success, as might be expected; others, of a mechanical kind, with partial success, as the introduction of a certain quantity of sawdust into the boiler, or the application of tallow, or of a mixture of tallow and plumbago to its inside, to prevent close adhesion and the more easy separation of the incrusting matter either by percussion, using a chisel-like hammer, or by contraction and unequal expansion, by means of flame kindled with oakum, after emptying the boiler and drying it. Of all the methods hitherto used, that of "blowing off," that is the discharging by an inferior stop-cock a certain quantity of the concentrated water of the boiler by the pressure of steam, after the admission above of an equivalent quantity of sea-water of ordinary density, appears to be, from the reports made, the most easy in practice, the least unsuccessful and the most to be relied on. But, as in the instance given of the North American steamer, it can be viewed only as a palliation. Considering the composition of the incrusting matter and the properties of its principal ingredient, the sulphate of lime, a compound soluble in water and in sea-water, and deposited only when the water containing it is concentrated to a certain degree, there appears to be no difficulty theoretically in naming a preventive. The certain preventive would be the substitution of distilled or rain-water in the boiler for sea-water. Of this we have proof in the efficacy of Hall's condenser, which returns the water used as steam, condensed, after having been so used; but, unfortunately for its practical success, the apparatus is described as being too complicated and expensive for common adoption. Further proof is afforded in the fact, that the boilers of steamers navigating lakes and rivers in the waters of which there is little or no sulphate of lime, month after month in continued use, remain free from incrustation. This I am assured is the case with the steamers that have been plying several summers successively on the lake of Windermere. And it may be inferred, that in sea-going steamers, in which sea-water is used in the boiler, or indeed any water containing sulphate of lime, the prevention of deposition may be effected with no less certainty by keeping the water at that degree of dilution at which the sulphate of lime is not separated from the water in which it is dissolved.

From the few trials I have made, I may remark, that sulphate of lime appears to be hardly less soluble, if at all, in water saturated with common salt than in perfectly fresh water. This seems to be a fortunate circumstance in relation to the inquiry as to the means of prevention, and likely to simplify the problem. If these principles be sound, their application under different circumstances, with knowledge and judgement on the part of the directing engineer, will probably not be difficult. His great object will be in sea-going steamers to œconomize the escape of water in the form of steam,

and thereby also œconomize heat and fuel; also, when fresh water is available, to use it as much as possible: and further, to avoid using sea-water as much as possible near coasts and in parts of seas where sulphate of lime is most abundant.

From the incrustation on the boilers of sea-going steamers, the attention can hardly fail to be directed to that which often forms, to their no small detriment, in the boilers of locomotive railway engines, and of engines employed in mines and in the multifarious works to which steam power is now applied. These incrustations will of necessity be very variable, both in quantity and quality, according to the kind of ingredients held in solution in the water used for generating the steam. Hitherto I have examined two specimens only of incrustations taken from the boilers of locomotive engines, and a single one only from the boiler of a steam-engine employed on a mine, a mine in the west of Cornwall. The latter was fibrous, about half an inch thick, and consisted chiefly of sulphate of lime, with a little silica and peroxide of iron and a trace of fluorine. The former were from one-tenth of an inch in thickness to one inch. They were laminated, of a gray colour, and had much the appearance of volcanic tufa. They consisted principally of carbonate and sulphate of lime with a little magnesia, protoxide of iron, silica and carbonaceous matter; the last two, the silica and carbonaceous matter, probably chiefly derived from the smoke of the engine and the dust in the air. From the engineer's report, it would appear that the thinnest, the incrustation of about one-tenth of an inch, had formed in about a week, during which time the locomotive had run about 436 miles and consumed about 10,900 gallons of water.

On the Proportion of Phosphoric Acid in some Natural Waters. *By* Prof. Voelcker.

The object of this paper was to draw attention to a natural source from which many of our fields may be œconomically supplied with phosphoric acid. Prof. Fownes has shown that traces of phosphoric acid are met with in many rocks of igneous origin; but also in stratified rocks, particularly in limestone rocks, the presence of phosphoric acid has been indicated by several chemists. The author found the proportion of phosphoric acid in graptolite, from the neighbourhood of Cirencester, amounting to 0·124 per cent., equal to 0·260 of bone-earth; and in Stonesfield slate, from the same locality, amounting to 0·117, equal to 0·244 per cent. of bone-earth. As water, charged with carbonic acid, is capable of dissolving bone-earth, this important fertilizing substance is found in many natural waters, percolating rocks which contain phosphoric acid. Such waters therefore may be applied with advantage for irrigation. The advantages derived from this too often neglected natural source are strikingly exhibited in the irrigated meadows in the neighbourhood of Cirencester; and it is the opinion of the author that one of the chief causes of the beneficial effects which follow the application of

the water for irrigation in this locality is to be found in the phosphate of lime it contains. In a tea-kettle incrustation, formed in a short period by this water, the proportion of phosphoric acid was found to amount to 1·25 per cent., showing a considerable quantity of this acid present in the water. A very hard water from Edinburgh likewise proved to contain phosphoric acid; but its proportion was not so large as that in the Cirencester water, the quantity of phosphoric acid in a boiler incrustation formed by this Edinburgh water being only 0·427 per cent. Sea-water also contains phosphoric acid, but the proportion of the latter amounts to mere traces. A quantitative determination of phosphoric acid in the boiler deposit of a Canada steamer gave only 0·0306 per cent., and that in a boiler incrustation of a steamer plying between Dublin and Liverpool 0·0424 as the per-centage of phosphoric acid. In conclusion, the author recommended Svanberg's test, molybdate of ammonia, as a ready means for detecting the presence of phosphoric acid in natural waters.

On the Action of the Soap-test upon Water containing a Salt of Magnesia only, and likewise upon Water containing a Salt of Magnesia and a Salt of Lime. *By* DUGALD CAMPBELL, F.C.S.

Experiments were first made upon water containing a salt of magnesia alone in different proportions, in order to ascertain if the soap-test acted throughout with magnesian solutions as it does with lime. For this purpose, 19·2 grs. pure dry sulphate of magnesia (MgO, SO^3), the equivalent quantity of that salt to 16 grs. carbonate of lime, were dissolved in a gallon of distilled water. This solution was considered as a standard of magnesia of 16° hardness. Fifteen other standards were prepared from this by proportional dilution with distilled water in the same way as the standards of lime are recommended to be prepared by Professor Clark in the specification of a patent printed in the 'Repertory of Patent Inventions' for 1841.

The action of the soap-test in producing perfect lathers with these standards coincides, or nearly so, with the action of the soap-test upon like standards of lime up to the sixth degree; but from that point the magnesian standards begin not to require so much soap-test as the lime, and as the standards increase, this difference in soap-test increases till the magnesian standard of 16° requires only 19·6 soap-tests whilst the lime standard of 16° requires 32.

Standard solutions were prepared containing 16°, 12°, 8°, 6°, 4°, 2° lime in a gallon plus 1°, 2°, 3°, 4° magnesia, and so on up to 16°.

Less soap-test is requisite to cause a perfect lather in most of these solutions than is requisite for the standard of lime alone contained in them; or, in other words, the magnesia appears to soften the lime standards, and this peculiarity increases as the magnesia increases; for example, a standard of lime of 16° takes 32 test measures; a standard of lime of 16°+1° magnesia takes 31·6, and a standard of lime of 16°+16° magnesia, 27·9.

As the standards of lime decrease, the action of a few of the lower degrees of magnesia in softening is modified, till solutions of the standard of lime of 2° plus the first four degrees of magnesia take nearly as many soap-test measures as if they were entirely lime solutions.

In a number of these standard solutions, when a perfect lather had been produced by the minimum quantity of soap-test, the addition of a small quantity more reduced the lather to a curd; great agitation produced the lather again, and stronger than it was before the last addition of soap-test; if beyond a certain amount of soap-test however had been added, a new action showed itself, which was that the lather cannot be restored properly again until a certain amount of soap-test had been added; the additional quantities of soap-test were in every case noted when this peculiarity was observed.

The inferences drawn from the experiments are as follows:—

1. That water containing sulphate of magnesia alone acts towards the soap-test in producing with it a perfect lather, similarly or nearly so, as does water containing a lime salt alone, but only when the equivalent of magnesia salt does not exceed 6 grs. of carbonate of lime in a gallon of water.

2. That the degrees of hardness of an ordinary water cannot be inferred by the rule.—Compute the grains of lime, magnesia, oxides of iron, alumina, in a gallon of water, each into its equivalent of chalk. The sum of these equivalents will be the hardness of the water.

3. That the degrees of hardness of a water containing magnesia and lime salts, as shown by the soap-test as it is now applied, cannot in almost every case be taken as representing the amount of these salts in the water; nor, in nearly every instance, can it be considered as giving the amount of lime in a water when magnesia is present.

4. That water might show by the soap-test a small degree of hardness in comparison to the considerable quantities of salts of magnesia and of lime it might contain, and trusting to this method of analysis alone when selecting water for ordinary use and for steam purposes, might lead to a water being selected which might not be conducive to the general health, and which would leave considerable deposit in vessels in which it was boiled,—a great deterioration to its use in steam generating.—*Abstract communicated by the Author.*

On the Presence of Carbonates in the Blood. *By* Prof. Mulder.

The intention of Prof. Mulder was to show experimentally that blood contains carbonic acid not merely in solution, but also in chemical combination with bases and organic substances, as globuline, albumen, &c.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of Atropine, Daturine and Aconitine. *By* Dr. A. von Planta.

Atropine.—The atropine used by the author for these researches was prepared by Merck, and possessed the following properties :— It dissolved in 299 parts of water at the ordinary temperature; dissolved in almost every proportion in alcohol, but less readily in æther; in both liquids, as well as in water, the solubility is increased by heat. It fused at 194° F. to a clear transparent mass, which became brittle on cooling; on the reapplication of heat, and again allowing it to cool, it was converted into stellate groups of crystals. At 284° a portion is volatilized undecomposed, but the greater portion is destroyed. Heated upon platinum foil, it melts, puffs up, giving off white fumes, and burns with a bright flame, leaving a shining black cinder, which finally disappears entirely.

Atropine has a strong alkaline reaction, and combines with acids, forming salts, which appear mostly not to crystallize; they are soluble in water and alcohol, but very sparingly in æther, especially the muriate and sulphate. On pouring a concentrated alcoholic solution of the muriate into æther, a syrupy solution separates, which did not crystallize after long standing in ice, nor was it possible to obtain the neutral muriate of atropine crystallized by retaining it for several days at a temperature of 86°–104°. The solution of the muriate of atropine furnishes pulverulent precipitates with potash, ammonia and carbonate of potash, but only with very concentrated solutions, and they dissolve very readily in an excess of the reagent. Carbonate of ammonia, bicarbonate of soda and phosphate of soda give no precipitates; perchloride of gold produces a sulphur-coloured crystalline precipitate, which is sparingly soluble in muriatic acid; chloride of platinum gives a pulverulent precipitate, which cakes together like a resin and is very readily soluble in muriatic acid. The sodio-chloride of iridium gives no precipitate; perchloride of mercury gives one, but only in very concentrated solutions. The potassio-iodide of mercury produces a very heavy, whitish, caseous precipitate, which contracts considerably upon the addition of muriatic acid. Iodide and sulphocyanide of potassium give no precipitate; tincture of iodine strikes a kermes-brown colour; iodic acid, in the cold, no colour. With tincture of galls, a dense flocculent precipitate is ob-

tained, but only after the addition of muriatic acid, in the excess of which it dissolves somewhat. Nitropicric acid produces a sulphur-coloured pulverulent precipitate; nitric acid causes no change either alone or on the addition of protochloride of tin.

Atropine, dried under the air-pump, furnished—

	I.	II.	III.			
Carbon.....	70·22	69·72	70·74	34	=204	70·58
Hydrogen....	8·37	8·00	8·31	23	23	7·95
Nitrogen	5·26	5·26	5·26	1	14	4·84
Oxygen.....	16·15	17·02	15·69	6	48	16·60
	100·00	100·00	100·00		289	100·00

These analyses agree very well with those previously made by Liebig.

Auro-chloride of Atropine, $C^{34}H^{23}NO^6 + HCl + AuCl^3$.—This compound is obtained by pouring a concentrated solution of atropine in muriatic acid, drop by drop, into a dilute solution of chloride of gold. The precipitate, which is at first pulverulent, is very soon converted into a thick paste of crystals of a yellow colour. The auro-chloride of atropine is sparingly soluble in water, and can therefore be easily washed; it experienced no loss in weight under the air-pump either at 212° or at 248°; at 275° it began to melt. The analysis furnished—

Carbon	31·50	32·07	34 =	204·00	32·45
Hydrogen	3·85	4·12	24	24·00	3·81
Nitrogen.....	..	..	1	14·00	2·22
Oxygen	..	..	6	48·00	7·63
Chlorine	..	..	4	141·84	22·56
Gold	31·39	31·39	1	196·66	31·29

Daturine, $C^{34}H^{23}NO^6$.—The analysis of daturine led the author to the remarkable result, that daturine is identical with atropine. The preparation examined consisted of fascicles of colourless bright needles; it was heavier than water, not altered by exposure to the air, perfectly free from smell, and scarcely soluble in water. It dissolved more readily in alcohol than in æther, but in both liquids its solubility was increased by heat. At 190° F. it melts without decreasing in weight; on cooling, it furnishes, like atropine, a brittle, colourless, transparent mass, which at a higher temperature is partially volatilized unaltered. It melts upon platinum, puffs up, giving off white vapours, and burns with a bright luminous flame, leaving a shining black cinder, which at last entirely disappears.

Daturine has a strong alkaline reaction, and forms salts with acids. In the present case it was likewise found impossible to obtain the sulphate and muriate crystallized. They are both readily soluble in water and in alcohol. The muriate of daturine furnishes pulverulent precipitates with potash, ammonia and carbonate of potash, but only with concentrated solutions; the precipitates dissolve easily in an excess of the reagent. Carbonate of ammonia, bicarbonate and

phosphate of soda give no precipitate; perchloride of gold produces a sulphur-coloured crystalline precipitate, which is slightly soluble in muriatic acid; chloride of platinum, with very concentrated solutions, gives a precipitate, which is at first pulverulent, but soon cakes together like a resin, and then no longer dissolves so readily in muriatic acid. Perchloride of mercury produces a white pulverulent precipitate only in very strong solutions; it is readily soluble in muriatic acid and in chloride of ammonium; no precipitate is produced by sulphocyanide of potassium; tincture of iodine gives a kermes-coloured flocculent precipitate, which soon turns blackish-blue; tincture of galls and tannic acid cause a copious precipitate only on the addition of muriatic acid; that produced by the first reagent dissolves with difficulty in the excess of muriatic acid; that by the second, readily. Nitropicric acid furnishes a yellow precipitate, which is easily soluble in ammonia.

The daturine for analysis was dried under the air-pump; the results do not agree perfectly with the calculation, owing to the presence of a little impurity, which was subsequently detected:—

Carbon	69·04	69·30	69·55	34	=204	70·58
Hydrogen	8·04	8·12	7·86	23	23	7·95
Nitrogen.....	4·94	4·94	4·94	1	14	4·84
Oxygen	17·98	17·64	17·65	6	48	16·60
					289	

Auro-chloride of Daturine, $C^{34}H^{23}NO^6 + HCl + AuCl^3$, is obtained in the same manner as the corresponding salt of atropine; it is of a beautiful yellow colour, sparingly soluble in water, and may therefore be easily washed. It experiences no loss in weight under the air-pump at 149° F.; between 194° and 212° it fuses and turns brown; it is not decomposed at 320°. The analysis gave—

Carbon	32·75	34 =	204·00	32·45
Hydrogen	4·43	24	24·00	3·81
Nitrogen.....	..	1	14·00	2·22
Oxygen	..	6	48·00	7·63
Chlorine	..	4	141·84	22·56
Gold	31·36	1	196·66	31·29
			628·50	100·00

The identity of atropine and daturine is especially evident from the following analyses of the gold salts, made with chromate of lead and oxygen:—

	Atropine.	Daturine.			
Carbon	32·75	32·75	34 =	204·00	32·45
Hydrogen	4·12	4·43	24	24·00	3·81
Nitrogen.....	..	..	1	14·00	2·22
Oxygen	..	..	6	48·00	7·63
Chlorine.....	..	..	4	141·84	22·56
Gold	31·3	31·3	1	196·66	31·29
				628·50	

Aconitine.—The aconitine employed in this investigation, after being purified by the author, formed a colourless powder, without smell and not altered by exposure to the air; heated upon platinum, it melted very readily, took fire, and left a shining black cinder, which was entirely consumed. It cannot be volatilized like daturine and atropine. Aconitine is heavier than water; it dissolves very easily in alcohol, less so in æther; it melts at 176° F. to a transparent vitreous mass without losing in weight; at 248° it begins to turn brown, and is decomposed at a higher temperature. It has a strong alkaline reaction, completely neutralizes acids, but the salts do not crystallize. The muriate of aconitine furnishes, with potash, ammonia and carbonate of potash, a white flocculent precipitate of aconitine, which is slightly soluble in an excess of the reagent. No precipitate is produced by carbonate of ammonia, bicarbonate of soda or phosphate of soda. Chloride of gold gives a dense yellowish precipitate, which is not perceptibly soluble in muriatic acid; chloride of platinum gives no precipitate. With perchloride of mercury and sulphocyanide of potassium white caseous precipitates are obtained; that formed by the first reagent dissolves without difficulty in muriatic acid and chloride of ammonium. Tincture of iodine produces a kermesine-brown; tincture of galls and tannic acid, upon the addition of a drop of muriatic acid, a dense flocculent precipitate, which requires much muriatic acid for its solution. Nitropieric acid gives a yellow precipitate, insoluble in ammonia. The analysis of aconitine, dried under the air-pump, furnished—

	I.	II.	III.			
Carbon	67·81	68·34	67·75	60	=360	67·54
Hydrogen	8·82	8·90	8·64	47	47	8·81
Nitrogen.....	3·42	3·42	3·42	1	14	2·62
Oxygen	..	..	..	14	112	21·01
					533	

Auro-chloride of Aconitine, $C^{60}H^{47}NO^{14}+HCl+AuCl^{3}+2HO$, is obtained in the same way as the corresponding salts of atropine and daturine; it is amorphous, and furnished on analysis—

	I.	II.			
Carbon	40·23	40·42	60	= 360·0	40·44
Hydrogen.....	5·64	5·54	50	50·0	5·61
Nitrogen	..	..	1	14·0	1·57
Oxygen.....	..	..	16	128·0	14·38
Chlorine	..	..	4	141·8	15·93
Gold.....	22·06	22·06	1	196·6	22·08
				890·4	

It follows from this that the atomic weight of aconitine is 533·66. The muriate of aconitine, prepared by passing muriatic gas at 212° over aconitine, contanied 13·41 per cent. of muriatic acid. According to which we have—

		Found.	Calculated according to $C^{60}H^{47}NO^{14}+2HCl$.
1 equiv. aconitine.....	533	86·59	87·16
2 equivs. muriatic acid.....	72·92	13·41	12·84
1 equiv. bimuriate of aconitine	605·92	100·00	100·00

Liebig's *Annalen*, lxxiv. p. 245.

On the Colouring Principle of Sandal-Wood.
By A. Weyermann *and* E. Hæffely.

The examination of sandal-wood recently published by L. Meier* induced us to prepare the colouring principles described by him, in order to submit them to elementary analysis. Pelletier was the first who obtained the pigment santaline from sandal-wood, and assigned to it the formula $C^{18}H^{8}O^{3}$. Preisser, in his dissertation "On the Origin and Nature of the Organic Colouring Matters†," examined this substance, and states that he obtained it colourless, which has since been refuted by Bolley‡. The latter chemist exhausted a pale kind of sandal-wood with alcohol, and precipitated the solution with water; he found in the substance prepared in this manner 67·2 per cent. of carbon and 5·6–6·0 per cent. of hydrogen; in that obtained in the same manner from a darker wood, 65·3–66·2 per cent. of carbon and 5·4–5·6 hydrogen. From the paler sort, by treatment with potash, precipitating with muriatic acid, dissolving the precipitate in alcohol, and reprecipitating with water, he obtained a preparation which furnished 64·3–64·7 carbon and 4·9–5·3 hydrogen. The combinations of this colouring principle with oxide of lead prepared by Bolley furnished variable quantities of oxide of lead.

Meier finds in sandal-wood a resinous acid, *santalic acid*, which is said to constitute the peculiar colouring principle, a pigment which he calls santalic oxide, and four other substances, to which he gave the names of santalide, santaloide, santalidide and santaloidide. The four last mentioned substances are said to occur in the aqueous extract of sandal-wood; we did not trouble ourselves with their preparation, as we obtained by treating several pounds of sandal-wood with boiling water, and evaporating the solution, a gummy substance, which contained little colouring matter, and the amount of which, in comparison with that of the wood employed, was very small.

To prepare the santalic acid, Meier exhausts the sandal-wood with alcohol, evaporates the solution to dryness, exhausts the resinous substance obtained with boiling water, and dissolves it again in alcohol. This solution is mixed with an alcoholic solution of acetate of lead, when a dark violet precipitate, santalate of lead, falls, from which the acid is obtained in red scales by decomposition with sul-

* Chem. Gaz., vol. vii. p. 130. † Ibid., vol. ii. p. 371.
‡ Ibid., vol. v. p. 423.

phuric acid. From the liquid filtered from the santalate of lead, Meier prepares the so-called santalic oxide.

We found the santalic acid prepared according to Meier's directions to possess in general the properties he has ascribed to it. It is insoluble in water, easily soluble in alcohol; the solution is blood-red, and reddens blue litmus; alkalies dissolve it readily, acquiring a dark violet colour; hot acetic acid and concentrated sulphuric acid likewise dissolve it. The combinations of the acid with baryta and lime are almost insoluble in cold water. Prepared according to Meier's directions, the acid still leaves on combustion a large quantity of ash; we obtained it perfectly free from inorganic constituents by mixing the alcoholic solution with a little muriatic acid, and precipitation by water. The acid, so purified, was again dissolved in alcohol, when it separated on evaporation as a crystalline red powder, which, dried at 212°, and burnt with oxide of copper, furnished—

Carbon	65·8	65·9	30 =	180	65·7
Hydrogen	5·2	5·2	14	14	5·1
Oxygen	29·0	28·9	10	80	29·2

Santalate of lead prepared by mixing the alcoholic solution of santalic acid with an alcoholic solution of acetate of lead, and edulcoration of the precipitate with alcohol, gave, after being dried at 212°,—

Carbon	37·0	35·3	30 =	180	36·2
Hydrogen	2·8	2·8	14	14	2·8
Oxygen	15·6	17·0	10	80	15·6
Oxide of lead	44·6	44·9	2	223·2	44·5

Santalic acid dissolves readily and completely in an aqueous solution of ammonia; this solution was precipitated with chloride of barium, and the dark violet crystalline salt obtained washed with water, excluding the air as much as possible; it furnished, after being dried at 212°,—

Carbon	53·2	53·7	30 =	180	52·7
Hydrogen	4·6	3·5	13	13	3·8
Oxygen	19·3	19·9	9	72	21·1
Baryta	22·9	22·9	1	76·5	22·4

In calculating the analysis, it was assumed that the whole of the baryta remained after the combustion as carbonate, but probably a portion had parted with its carbonic acid, which will perhaps explain the difference in the amount of carbon.

With respect to Meier's so-called santalic oxide, we were unable to obtain any substance resembling it from the liquid filtered from the santalate of lead either by his or by any other method. On evaporating the liquid, after removal of the lead by a current of sulphuretted hydrogen, we obtained a coloured resinous body, and tried to decolorize it by ebullition with animal charcoal; this however was more perfectly accomplished by precipitating with an alcoholic solution of acetate of lead, which carries down the colouring substance sooner than the resin. By dissolving the decolorized resin in absolute alcohol and spontaneous evaporation, we obtained colour-

less silky crystals, which puffed up like a resin on combustion, and left not the least trace of residue. On heating these crystals in water, they melt at about 140° into globules, and then become diffused in the water, giving it a milky appearance. This substance has no reaction upon litmus, and is insoluble in acid and in alkalies. It contains no nitrogen.—Liebig's *Annalen*, May, p. 226.

On Githagine. *By* E. A. Scharling.

Nearly seventeen years ago I undertook an examination of the seeds of the corn cockle, *Agrostemma Githago*. The memoir upon them was not however published then, nor has it been since, mainly because I had not sufficient material at my command to enable me to illustrate satisfactorily the properties, composition, compounds and metamorphoses of a peculiar constituent which I obtained, and denominated agrostemmine. Nor should I on the present occasion have published anything regarding the investigations then made, had not another chemist, Schultze, made a brief communication in the 'Archiv der Pharmacie,' lv. and lvi.*, regarding two preparations of a substance, which he had separated from the seeds of the corn cockle, and also named agrostemmine. As the attention of others has thus been directed to the examination of the constituents of these seeds, I think that at least an abstract of my former experiments ought not to be kept back any longer, especially as my results differ from those of Schultze in several respects.

Agrostemma Githago has been regarded as a noxious plant from the earliest times, and in various botanical writings are contained numerous experiments upon the poisonous effects produced by its seeds upon different animals. But the fact is not so well known, that the seeds, when ground into meal and mixed with water, may be used for cleansing white woollen stuffs, and that they produce a more active fermentation when mixed in large quantity with the corn usually used in the preparation of brandy. For the sake of investigating the latter property more accurately, I undertook, about seventeen years ago, an analysis of the seeds of the corn cockle, as also some experiments upon fermentation, in consequence of which I ascribed the more active fermentation which the seeds were capable of producing to the vegetable gelatine they contained. The poisonous effects of the seeds were found to exist in a greater degree in a peculiar substance, which, to distinguish it from Schultze's agrostemmine, I shall call *Githagine*.

Githagine exists in the seeds mixed with a fatty oil, vegetable gelatine, sugar, gum, starch, vegetable albumen, the usual salts found in most plants, and with various other substances which have not been accurately determined. Several methods of procuring githagine have been used, a few only of which I shall mention here. The seeds, ground into meal, are carefully dried, and then repeatedly digested with æther to extract the fatty oil. The residue is digested with alcohol of 0·826, by which more of the oil and the

* Chem. Gaz., vol. vii. p. 197.

æther remaining in the meal are removed. After this treatment, the meal is repeatedly boiled with alcohol of 0·852, the liquids filtered, and then subjected to distillation to separate the alcohol. The residue is then perfectly dried, and exhausted with boiling alcohol of 0·826. The solutions are filtered whilst as hot as possible, and set aside to cool. A white substance then separates, which is impure githagine. Absolute alcohol separates a further portion of the githagine from the supernatant liquid. This githagine is collected, dried, and dissolved in water; a substance then separates, which I regard as a kind of vegetable gelatine. The solution filtered from it is treated with a solution of acetate of lead; a precipitate is then formed, which is separated by filtration, and the filtered liquid is completely precipitated with basic acetate of lead. A compound of githagine and oxide of lead is then precipitated, which is carefully washed, stirred with water, and decomposed with sulphuretted hydrogen. After the separation of the sulphuret of lead by filtration, the clear liquid is evaporated in a water-bath. At a certain period of the latter operation, the formation of a gelatinous mass is perceived*. The evaporation is then discontinued, the mass filtered after cooling, and the filtered liquid further evaporated or placed over sulphuric acid to dry. The githagine thus obtained forms a brittle yellowish-brown mass, resembling gum. On precipitating a concentrated aqueous solution of it with strong alcohol, the githagine is obtained in the form of a white mass, resembling starch. Another method which I adopted consisted in dissolving the extract prepared from the seeds in water, and boiling the filtered solution with calcined magnesia. The solution was then again filtered, evaporated to a syrup and precipitated with alcohol. The githagine thus obtained was dissolved in boiling alcohol of 0·823, and the solution allowed to cool; it then subsided. The githagine obtained in this manner always left a little ash containing magnesia.

A similar result was obtained when I precipitated the aqueous solution of the corn-cockle seed with sulphate of copper, and separated the precipitate by filtration. The filtered liquid was freed from the copper by sulphuretted hydrogen, and digested with excess of carbonate of baryta after filtration, to remove the sulphuric acid. To separate the barytic salt as perfectly as possible, the liquid was mixed with alcohol and filtered. The liquid was then either precipitated with strong alcohol after sufficient concentration, or evaporated to dryness, and the residue boiled with alcohol of 0·823. The githagine separated on cooling, but in this case it always contained a little baryta.

The githagine which has separated from an alcoholic solution on cooling, or that precipitated by absolute alcohol from a solution, forms when dried larger or smaller pieces, which in appearance and point of brittleness resemble starch, but having however somewhat of a silky lustre, and under a powerful microscope exhibit a crystal-

* When dried, this body appeared under the microscope to consist of a mechanical mixture of an organic substance with crystals of a salt; and when incinerated upon platinum foil, it left a considerable amount of ash.

line fracture. When exposed for several hours to the action of a current of dry air at 212° F., it presents on cooling an interesting phænomenon, in the violence with which the larger pieces burst and fly into smaller pieces. In an experiment to determine whether it had thereby experienced any loss of weight, the scale-pan was set in vibratory motion by the force with which the pieces separated from each other, and innumerable small pieces of it were projected from the pan in which the githagine was being weighed.

When an alcoholic or an aqueous solution of githagine is evaporated to dryness, either *in vacuo* or under a bell-glass with sulphuric acid, a clear somewhat yellowish-brown mass resembling gum-arabic is obtained, which appears amorphous under the microscope. On one occasion only have I obtained real crystals of githagine, and this was when I had allowed an alcoholic solution of it to remain for a year in a cylindrical glass vessel, which, to prevent rapid evaporation, had been covered with printing paper and a funnel. On the point of the funnel a few acicular crystals were found at the end of the above period; these left no trace of ash on incineration.

In the dry state githagine may be kept for many years without absorbing enough moisture to cause it to lose its brittleness and easy pulverizability. It is not perceptibly dissolved by either cold or boiling absolute alcohol or æther. However, it dissolves in boiling spirit of 0·823, and on cooling a part only separates. Weaker spirit dissolves it readily, and water still more readily.

Githagine is inodorous so long as it retains the solid form, whilst its aqueous solution, which upon the slightest agitation froths very strongly, possesses a disagreeable nauseous odour. Its taste is at first scarcely perceptible, but subsequently a disagreeable burning sensation is gradually produced on the palate. When a drop of the aqueous solution gets into the eye, a violent burning pain is produced and the pupil is dilated. Neither the aqueous nor the alcoholic solution exerts any perceptible action upon vegetable colours. Although githagine takes up small quantities of dilute acids, still it does not appear to form any definite chemical compounds with them. Concentrated sulphuric acid produces a red colour with githagine similar to that with salicine, but the margins of the liquid are somewhat bluish. If the red liquid be exposed to the air, the red colour gradually disappears, and a bluish green colour replaces it, which is very distinct even at the end of twenty-four hours.

If githagine is boiled with a mixture of alcohol of 0·848 and a little dilute sulphuric acid, gradually and in proportion as the alcohol evaporates a gelatinous mass is obtained, which is only imperfectly dissolved by a large quantity of boiling water, but is very easily dissolved by alcohol. If 1 part of githagine be boiled with from 6 to 8 parts of concentrated nitric acid, a lively evolution of red vapours occurs; and when these have been very intense, a solid yellow body separates, which swims upon the surface of the liquid. This substance is almost insoluble in water, but readily soluble in alcohol. On the evaporation of this solution, a yellow uncrystallized body separates. Ammonia colours the alcoholic solution yellowish-brown

without troubling the liquid. On carefully examining the acid fluid from which the above-mentioned body had separated, it was found to contain oxalic acid and a little nitrate of ammonia.

On incinerating githagine upon platinum foil, a small quantity of ash was almost always obtained, the constituents of which varied according to the method adopted to procure the githagine. When heated in a glass tube closed at one end, it evolves a perceptible quantity of ammonia. An aqueous solution of githagine is precipitated by basic acetate of lead, and an alcoholic solution is precipitated by a solution of nitrate of silver in alcohol. Bichloride of platinum, pernitrate of mercury, bichloride of mercury and tannic acid, however, produce no precipitate either immediately or at the end of twenty-four hours. We must however remark, that impure githagine, as directly obtained by boiling the liquid left after decomposing the compound of githagine and oxide of lead with sulphuretted hydrogen, is precipitated by tannic acid.

When the solution is treated with potash and sulphate of copper, a bluish-green precipitate is formed, but there is no perceptible reduction.

My experiments to determine the elementary composition of githagine have not led to any satisfactory result, because, although the analyses which were made of one preparation of githagine agreed very well together, they did not with those of githagine of different preparations. Neither could any compounds of githagine with inorganic bodies be obtained in such definite proportions as are requisite to determine its atomic weight.

Githagine possesses in an eminent degree the poisonous action which the corn-cockle seeds exert upon animal life. A few drops of a solution of 3 grs. of githagine in a drachm of water acted powerfully upon a Canary bird. White froth issued from its beak, it fell down, and its whole body trembled, and on the following morning it was dead. When opened, none of the internal parts were inflamed. The auricle of the heart was filled with blood, whilst the ventricles were empty. In the intestines there was a considerable quantity of a yellowish-green liquid, indicating a considerable secretion of bile.

A pigeon, into the mouth of which in the morning I injected a solution of $1\frac{1}{2}$ gr. of githagine, lost all desire for food and suffered from convulsions. It afterwards took a solution of 3 grs., which diminished its vital powers very greatly. It let the wings drop, the eyes began to start from the head, and in a few hours it was dead.

A rabbit, into the mouth of which a solution of 10 grs. of githagine in a drachm of water was injected, was immediately seized with very violent convulsions, blood streamed from the nose and threatened to burst through the skin. The animal was dead in five minutes. On opening it, there was no mucus in the mouth; a little blood was effused in the lungs; prominent brown spots were observed here and there; the heart was unchanged.

To determine whether carnivorous animals were as powerfully attacked by it, a solution of githagine mixed with milk was given

to a cat; but although it was both hungry and thirsty, it hardly touched the milk, and tried to reject what it had taken of it, at the same time wheezing strongly. About 10 grs. of githagine, dissolved in the smallest possible quantity of water, were then injected into its mouth; it immediately began to foam and to throw up white mucus. In six hours' time another similar portion was given to it. The same effect was produced, excepting that the eyes became very dull; in twenty-four hours' time the appearance of the cat was very much changed, and it died on the eighth day. On opening the animal, the pericardium was found to contain water; the intestines were inflamed, and exhibited distinct signs of poisoning.

$2\frac{1}{2}$ grs. of githagine were given to two poodle dogs, a little sulphuric acid being added to it in one case. They merely evinced some efforts to vomit. They were subsequently both given larger doses; these produced more powerful efforts at vomiting, which also continued for some time afterwards. 10 grs. of githagine dissolved in 3 drachms of water, immediately produced very violent vomiting in one of the dogs. After some hours, during which it had vomited many times, it recovered itself, and was very well afterwards. The experiments upon the cat and the dogs were made in the Royal Veterinary School, where similar experiments were formerly made with the seeds of the corn cockle. These older experiments, which are detailed in Rafn's 'Danmark og Hosteens Flora,' ii. 786, conjoined with those now detailed, leave no doubt that the injurious effects of the corn-cockle seeds upon animal life are partly produced by the githagine.

Future experiments must show what relation the githagine here mentioned holds to the agrostemmine of Schultze.—*Ann. der Chem. und Pharm.*, vol. lxxiv., p. 351.

On some new Salts of the Organic Alkaloids.

By G. W. Elderhorst.

[Continued from page 329.]

Urates.

Urate of Cinchonine is formed when uric acid is boiled with an excess of recently-precipitated cinchonine for a long time with much water, and filtered while hot. It crystallizes in prisms 3 or 4 lines in length, among which are perceived numerous twin-crystals, resembling those of harmotone. It is rather sparingly soluble in water, hot alcohol and æther. It is carbonized by heat, giving off the products of decomposition of cinchonine and of uric acid.

This salt exhibits a remarkable character in the drying, both by heat and at the ordinary temperature over sulphuric acid. The transparent crystals become opake, and fall to a white powder, which finally assumes a beautiful sulphur colour. On observing this change under the microscope, the same phænomenon is apparent as in the case of the yellow periodide of mercury; an incessant motion is perceived in the crystals, which become converted

into an innumerable quantity of minute crystals, undoubtedly of a different form. Frequently indeed some of the latter are seen to shoot forth from the lateral facets of the primitive crystals with a certain violence. With a tolerable amount of crystals, this state of motion is perceptible to the naked eye.

0·5388 grm. of air-dried salt lost, at 212°, 0·074, or 13·73 per cent. of water. No further loss in weight occurs at a higher temperature, but at 356° it begins to be destroyed.

0·6105 of the salt dried at 212°, digested with a mixture of concentrated muriatic acid and alcohol, and the separated uric acid dried upon a weighed filter at 212°, furnished 0·2235 hydrated uric acid, corresponding to 32·69 per cent. in the anhydrous state. In a second experiment, 32·47 per cent. was obtained. The solution of cinchonine filtered from the uric acid was mixed with chloride of platinum and æther (in order to render the double salt more insoluble). After washing, drying and ignition, it left 0·353 platinum, corresponding to 64·89 per cent. of cinchonine. According to these results, the salt dried at 212° is anhydrous neutral urate of cinchonine, $C^{20}\,H^{12}\,NO\,HO + C^{5}\,H\,N^{2}\,O^{2}$, which requires 64·72 per cent. cinchonine and 31·50 dry uric acid. The crystallized salt contains 4 atoms, or 12·49 per cent. of water.

Urate of Quinine, prepared in the same manner, could not be obtained crystallized. The solution dries to a white, laminar, amorphous mass.

Urate of Morphine is obtained by boiling uric acid and morphine with water. From the boiling filtered solution the salt crystallizes in short, somewhat brownish, concentrically-grouped prisms. It could not be recrystallized without decomposition, and separates as an amorphous brown pellicle.

Oxalurates.

Oxalurate of Cinchonine is obtained by saturating a boiling solution of parabanic acid with an excess of cinchonine. The solution dries to a yellowish transparent mass, which gradually becomes white and crystalline. Muriatic acid separates pulverulent oxaluric acid from it. On ebullition with muriatic acid, it dissolves, with formation of oxalic acid.

Oxalurate of Strychnine.—This salt does not appear to exist; at least it could not be produced by boiling strychnine with a solution of parabanic acid. From the hot filtered solution, long, flat, yellowish prisms crystallized, which were found to be *oxalate* of strychnine. Their solution was precipitated with acetate of lead, and the washed precipitate decomposed with sulphuretted hydrogen. Pure crystallized oxalic acid was obtained from the solution. On analysis it afforded 69·20 C and 6·56 H; the neutral oxalate of strychnine, $C^{44}\,H^{23}\,N^{2}\,O^{8}$, requires 69·84 C and 6·07 per cent. H.

The crystalline salt contains 4 atoms of water or 9·51 per cent. 0·3977 air-dried salt lost, at 302°, 0·0392 = 9·88 per cent. The crystals become white even at 212°.

It must therefore be admitted that the oxalurate of strychnine is

instantly decomposed on heating its solution into oxalate of strychnine and oxalate of urea.

Cyanurates.

Cyanurate of Cinchonine was prepared by dissolving recently-precipitated cinchonine in a boiling saturated solution of cyanuric acid. The solution, filtered from the excess of cinchonine, deposits the salt in flat four-sided oblique prisms. It is very sparingly soluble in water and insoluble in alcohol and æther. The salt lost 17·79 per cent. water at 212°, and likewise the same amount over sulphuric acid. At 392° no further loss results, but at that temperature it is decomposed with evolution of vapour smelling of oil of bitter almonds.

Cyanurate of Quinine is white and amorphous, and could not be crystallized from water or alcohol.

Cyanurate of Morphine was obtained in concentrical groups of colourless narrow prisms, about half an inch in length, but always associated with crystals of cyanuric acid even when an excess of morphine was employed. On recrystallization it was decomposed, with formation of a white amorphous mass.

Hippurates.

Hippurate of Strychnine.—A saturated boiling solution of hippuric acid neutralized with strychnine does not crystallize. On evaporation it forms a syrup, and subsequently a tolerably hard, amorphous, transparent mass, which turns white and solid after the lapse of several months, and then consists of verrucoid masses of microscopic needles. Muriatic acid separated from a concentrated solution a mixture of crystals of hippuric acid and muriate of strychnine.

Hippurate of Morphine does not appear to crystallize. The solution forms a syrup on evaporation, and then congeals to a hard, transparent, amorphous mass.

Hippurate of Cinchonine is likewise amorphous. The solution first forms a syrup, and then hardens to a transparent mass. Muriatic acid separates crystals of hippuric acid from the solution, and ammonia precipitates cinchonine.—Liebig's *Annalen*, lxxiv. p. 77.

Poisonous Effects from Zinc.

It is now some time since it was proposed by M. Leclaire to use oxide of zinc as a substitute for white lead, with a view to avoiding the dangerous effects of the latter on the workmen. There could be little doubt that, in point of salubrity, oxide of zinc was an improvement on carbonate of lead; but it was still a matter worth determining to what extent the oxide of zinc was itself free from objection, and whether or not some precautions were necessary regarding its use.

M. Flandin endeavoured to determine this experimentally. He rubbed animals over with ointments of oxide of zinc, of carbonate

of lead and sulphate of lead; and whilst he found that the two last always produced poisonous effects, he observed that the animals rubbed over with the oxide of zinc continued to enjoy their usual health. The following facts however show that the innocuousness of oxide of zinc must not be admitted so decidedly as Flandin supposes:—

I. *Poisoning by Oxide of Zinc, used as a substitute for White Lead.* By Dr. Bouvier, of the Hôpital Beaujon.—A man, aged 42, a labourer, entered on 19th April with all the symptoms of metallic colic. He had been employed for the fifteen previous days at a white colour manufactory, along with five other workmen, in barrelling oxide of zinc, and in repairing casks which had contained that substance, during which operation they were exposed to an atmosphere loaded with the powder of the oxide. From the commencement of their work he and his comrades experienced colic and a repugnance to food, and the wine and brandy which they took to excite their appetite were disgusting to them, and did not remove the clammy taste which they had constantly in their mouths. This man could not continue long at work. After ten days of this employment, he was seized with vomiting, severe colic, accompanied by constipation, which persisted and increased in intensity so much that he rolled on the floor in agony. On the day of admission he continued to vomit, and to suffer severe abdominal pain. The vomited matters were bilious, and he rejected all his food almost immediately after swallowing it; he had had no stool for five days; the belly otherwise was natural, the tongue whitish; he had no appetite, was free from fever, but was sleepless. The next day, 20th April, the bowels were opened by 2 oz. of sulphate of magnesia and the painter's purgative clyster, as used in La Charité (this consists of 12 oz. of wine with 6 of oil). The free evacuation of the bowels and the administration of $2\frac{1}{2}$ grs. of opium were followed by cessation of vomiting and diminution of the pain. From this time to 26th April, after having taken from 6 to 12 grs. of gamboge daily, and using frequent clysters and medicated baths, he became convalescent, and was dismissed cured on 4th May.

From the whole history of the case, there appeared to be no doubt that this man suffered from a genuine zinc colic. To ascertain that it was really oxide of zinc which had caused the illness, M. Bouvier collected, by washing the surface of his body, the metallic particles which adhere to it, and found them to consist of oxide of zinc. We are not entitled from this to say that the oxide of zinc is as noxious as white lead; but it shows, at least, that some precautions require to be taken by those who work with it in order to preserve their health.—*Compte Rendu de l'Académie des Sciences*, May 1850, in *Bulletin de Thérapeutique*.

II. *Zinc poisoning observed in the Workmen employed in twisting Galvanized Wire.* By MM. Landouzy and Maumené, of Rheims. —The iron wire employed for securing the corks of champagne is sent in bundles of 1 to 10 kilogrammes to workmen called *tordeurs*,

who by a dexterous manœuvre cut and twist from ten to twenty threads of wire at a time. These wires are then made up in packets of 1 kilogramme, and after being beaten with a bit of wood to make them even, are packed in bundles. Although this sort of work had been followed by the same workmen from eight to fifteen years under very bad hygienic circumstances as regards ventilation, they never had experienced any evil effects from it till the beginning of January 1850, when the so-called galvanized wire (which is iron wire covered with a layer of zinc) was substituted for the common iron wire; and soon after the workmen began to complain of the taste as of a sweetish powder in the throat, an incessant tendency to cough and spit, shiverings and general mal-aise. The whole of the people employed in this branch of industry—two youths, two women and two men—were affected by symptoms which were referable to zinc. Four had symptoms of general depression, with sore throat, swelling and ulceration of the tonsils, inflammation of the palate, white pellicles on the gums, salivation, fœtid breath, colic and diarrhœa. In one the colic and diarrhœa were the only symptoms observed; in another the colic was accompanied by nausea, tenesmus and obstinate constipation. The wires with which they worked had been made hurriedly and carelessly, and were covered with a dusty powder, which escaped abundantly during the twisting, and especially the beating of the wires. This powder consisted of zinc, oxide and carbonate of zinc, alloy of zinc and iron, iron and oxide of iron. It contained no trace of lead.

These symptoms seem to have subsided readily, without treatment, on abandoning the occupation. With one exception, all the work-people returned to their work in from three to six days.

That the symptoms were due to the exposure to the dust appears from the circumstance, that in fifteen days more the same work-people, in the same hygienic circumstances, resumed the same work, with the same galvanized iron, but free from all dust, and none of the phænomena, which were formerly observed, manifested themselves.—*Gaz. Méd. de Paris*, 1st June 1850.—*Edinburgh Monthly Medical Journal.*

On the Action of Nitric Acid upon the Organic Alkaloids. *By* Dr. T. Anderson.

When codeine is treated with very dilute nitric acid, nitrocodeine is obtained; if, on the contrary, the acid is moderately strong, a violent reaction takes place, with evolution of nitrous acid vapours, and an orange-coloured solution is formed, which deposits a resinous acid upon the addition of water. By expelling the nitric acid on the water-bath, the new acid is obtained in the form of a porous yellowish mass, readily soluble in alcohol, from which it is again precipitated by water. I have not yet completed the analysis of this substance; the results obtained however appear to point to a formula derived from that of codeine, by the substitution of NO^4 and the addition of several equivalents of oxygen. If this acid be treated

with a dilute solution of potash, it dissolves, furnishing a deep red liquid; and if heated to boiling, a volatile base of a very strong and peculiar odour is disengaged. On distillation, this base is contained in the water of the receiver. The liquid which passes over has a penetrating, and at the same time putrid odour, and diffuses white vapours when a glass rod moistened with hydrochloric acid is held over it. It has a strong alkaline reaction. The solution, saturated with hydrochloric acid and then evaporated on the water-bath, leaves a crystalline salt which dissolves readily in absolute alcohol. Bichloride of platinum added to the solution furnishes a beautiful yellow precipitate, which on analysis gave results corresponding to the formula $C^2 H^5 N, HCl, PtCl^2$; whence it results that the base is the methylamine of M. Wurtz. I had already established the formation of methylamine by the action of potash-lime and soda-lime upon codeine in a previous memoir. This base appears to be the sole product of the action of potash upon the yellow acid; but I have ascertained that the action of potash-lime upon codeine itself determines the formation, not only of methylamine, but likewise of another base, $C^6 H^{11} N$, propylamine*. A certain analogy appears therefore to exist between the action of soda-lime and that exerted successively by nitric acid and potash on this base.

Narcotine forms with nitric acid a great variety of products, which depend on the concentration of the acid. With a low temperature and a very dilute acid, derived bases are obtained, which I have not yet examined, but by the action of a stronger acid a yellow resinous acid is formed. When this is treated with a solution of potash, it disengages a volatile base, methylamine.

Morphine and Strychnine furnish, by the same treatment, volatile bases, which I am at present engaged in examining.

The action of nitric acid upon piperine is exceedingly violent; copious vapours of nitrous acid are disengaged, accompanied by an odour resembling that of bitter almonds. A brownish resin is formed, part of which floats on the surface, whilst the remainder is held in solution by the excess of nitric acid, from which it can be precipitated by the addition of water. On evaporating the excess of acid on the water-bath, a brown residue is obtained, which dissolves in potash with a magnificent blood-red colour. On ebullition, it disengages a volatile base of a peculiar and aromatic odour, forming with hydrochloric acid a beautiful salt, which crystallizes from absolute alcohol in needles an inch in length even when operating with very small quantities.

When nicotine is heated with nitric acid, a copious disengagement of red vapours results, and by adding an excess of potash a new volatile base is obtained, which appears to be ethylamine; but my experiments are not yet sufficiently advanced to enable me to state this positively.—*Comptes Rendus*, July 29, 1850.

* I may observe, that my experiments relating to the action of soda-lime upon codeine were made before I had read M. Wertheim's Note in the 'Anualen der Chem. und Pharm.' for February.

ANALYTICAL CHEMISTRY.

On a new Method of determining the Amount of Tin. *By* Ch. Mène.

Hitherto tin has always been determined in chemical analyses in the state of stannic acid. The great care and the time required in the manipulation, and the inevitable inaccuracy of the process, frequently deter from analyses of this metal. Having employed with success another method of determination, I consider it my duty to submit it to the examination of chemists. The new method is based upon the use of a normal solution, and is founded upon the property which the protochloride of tin possesses of removing chlorine from any body capable of furnishing it. When therefore a solution of the perchloride of iron, which is of a yellowish-red colour, is poured into one of protochloride of tin which is perfectly colourless, the salt of iron parts with 1 equiv. chlorine, converting the tin into perchloride, a colourless salt, and is now contained in the liquid in the state of protochloride, which is likewise colourless:—

$$Fe^2\,Cl^3 + SnCl = 2(FeCl) + SnCl?$$

The decoloration of the salt of iron must result therefore as long as the salt of tin requires chlorine; but as soon as the protochloride is entirely converted into perchloride, the least drop of the solution of iron will impart a lively colour to the test liquid, and will indicate the completeness of the operation. The strength of the solution of iron being known, the amount of tin sought for can be immediately ascertained.

This method of analysis is now so much in use, that I need only give the details necessary for the analysis of tin. For this purpose, from 1 to 2 grms. of the substance to be analysed is placed in a flask capable of holding about a pint with a mixture of 1 part nitric and 6 of hydrochloric acid, and boiled until the liquid acquires a yellowish colour and smells strongly of chlorine. The tin is now in the state of perchloride; some zinc is placed in the flask until the liquid becomes clear and colourless. The zinc in dissolving precipitates the tin in the metallic state, but the excess of hydrochloric acid immediately redissolves it, and retains it in the test liquid in the state of protochloride. The normal solution of the perchloride of iron is now added from a graduated burette until the colour remains permanent, and the proportion of tin is now determined by a simple calculation. It is advantageous to add a certain amount of water to the liquid under examination, especially when operating upon alloys which contain copper.

When the substance analysed consists of a mixture of tin and other metals, as copper, lead, &c., substances which are not or but slightly dissolved by hydrochloric acid, the zinc decolorizes the liquid and precipitates all of them in the metallic state, their particles unite at the bottom of the vessel and do not interfere with the reaction. When, on the contrary, the metals are such as are readily dissolved by hydrochloric acid, as iron, &c., they remain in the liquid

in the state of protochlorides and do not present any obstacle, as their affinity for chlorine is less than that of the tin and of the protochloride of iron. Arsenic alone forms an exception to this rule; when this is present, it is requisite to heat the alloy for some time in a coated crucible, the arsenic is then volatilized, and the tin which is left with the other mixed metals dissolves in the acid mixture as above.

The earthy bases, as lime, alumina and baryta, do not interfere in the process.

Before concluding, I will describe a convenient and short process for preparing the perchloride of iron, as it is important not to employ a salt which contains the least trace of free nitric acid; otherwise, in the analysis of the alloys of tin, it would act upon the other metals, oxidize them, and inevitably cause a loss. To prepare the perchloride of iron, I use the peroxide, but with greater advantage colcothar, which I boil for about ten minutes with pure hydrochloric acid, and filter immediately. This liquid may be kept for any length of time without alteration. The perchloride of iron may be crystallized by cooling and concentration; but the loss experienced, the variable and accidental products formed, and especially the uselessness of doing so, do not render the employment of the salt in crystals advisable. To ascertain the strength of a solution of perchloride of iron, 1 grm. of tin should be accurately weighed off, the number of divisions of the burette requisite to convert it into perchloride read off, and compared by calculation with the results of analysis.—*Comptes Rendus*, July 22, 1850.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Edinburgh, July 31st, 1850.

[Continued from page 348.]

On the Presence of Fluorine in Blood and Milk.

By Dr. G. Wilson.

In 1846 I announced to the Royal Society of Edinburgh, that, after finding that fluor spar was soluble in water, and occurred in many natural waters, I thought it well to seek for it in milk and in blood, and found distinct evidence of its presence in both. The proofs however were not so decisive as I could have wished. This summer, however, I have employed the fresh-drawn blood of the ox. About 24 imperial pints or 3 gallons of blood were made use of. From the large scale on which the experiment was conducted, and the simplicity of the process followed, the evidence in favour of the presence of fluorine in the blood of the ox seems unexceptionable; and it cannot be doubted that the blood of other animals will be found to contain the same element. I presume it to be present in the state of fluoride of calcium, and that its amount is very

small; but I have not attempted its quantitative determination. Milk was examined in a similar way, with 9 imperial pints of rich milk from a country farm. The vapour which they evolved etched glass distinctly. The ashes of 12 lbs. of new skim-milk cheese, made this spring, treated in the same way, occasioned deep etching of glass. The ashes of 4 imperial pints of whey, treated in the same way, have barely marked glass so as to show the faintest outlines when breathed upon. In all probability the fluoride of calcium is associated with the phosphate of lime, and when milk is coagulated, separates along with the caseine.

Dr. Wilson also stated, that he had repeated the inquiry into the solubility of fluoride of calcium in water, reported to the Association at its Southampton meeting, and with the same result, viz. that 16 fluid oz., or 7000 grs. of water at 60°, dissolve 0·26 gr. of fluor spar.

On a Compound of Iodine and Codeine. *By* T. Anderson, M.D.

The compound of iodine and codeine, which formed the special subject of this communication, is obtained by mixing together alcoholic solutions of equal quantities of codeine and iodine, and leaving the mixture to spontaneous evaporation, when the new compound is deposited in crystals. The compound is insoluble in water, sparingly soluble in cold alcohol, but readily in boiling, and it is again deposited in small triangular plates as the solution cools. Its crystalline form has been determined by Prof. Haidinger of Vienna, who finds it to belong to the doubly oblique system. The crystals have a fine diamond lustre and a deep purple colour by reflected, and ruby-red by transmitted light. In powder, its colour is cinnamon-brown.

PATENTS.

Patent granted to John Mercer *and* William Blythe, *for Improvements in certain Materials to be used in the Processes of Dyeing and Printing.*

This invention consists in manufacturing double salts in a solid or concrete state, composed of oxide of tin or stannic acid, and phosphoric, arsenic, or arsenious acid and soda, potash or ammonia, which may be called phospho-stannate of soda, arsenio-stannate of soda, &c.

These double salts are to be dissolved in water, and used for all the purposes for which stannate of soda has been heretofore employed in dyeing and printing cottons and other fabrics. All the double salts of phosphoric, arsenic or arsenious acid with stannic acid and soda, potash or ammonia, will answer; but the patentees prefer to employ the arsenio-stannate of soda. They make the solid or concrete arsenio-stannate of soda by adding arseniate of soda (made by fluxing or heating together equal weights of white arsenic and nitrate of soda) to stannate of soda in such proportions as will

form the strongest solid or concrete salt; this is about equal equivalents of arsenic and stannic acids. In 1 gallon of stannate of soda liquor at about 50° Twaddle's hydrometer, $1\frac{1}{2}$ lb. of arseniate of soda, made as above described, is dissolved in an iron vessel placed over a fire; a little of the thin mixture, while in a heated state over the fire, is taken out of the vessel and dropped on to a cold plate or stone; and if it immediately concrete into a solid, the fluid may be poured upon any suitable bed or receptacle, and will become solid as soon as cold; the substance thus produced is the solid or concrete arsenio-stannate of soda.

Phosphate of soda may be added to stannate of soda in the same way as the arseniate of soda, in order to produce phospho-stannate of soda; but the patentees do not confine themselves to the above mode of adding the arseniate or phosphate of soda; for the arseniate or phosphate may be added to the soda before the oxide of tin, or before the soda is made into stannate of soda. The arseniate of soda, arsenious acid or phosphate of soda may be added before, at the same time, or after the oxide of tin or stannic acid is united to the soda; and in each case the same arsenio-stannate or phospho-stannate of soda will be formed.—Sealed October 12, 1849.

Patent granted to John Scoffern, *for Improvements in the Manufacture and Refining of Sugar, and in the Treatment and Use of Matters obtained in such Manufacture.*

The improved mode of employing subacetates of lead for defecating saccharine solutions is as follows:—The juice having been put into a suitable vessel of copper or iron, heat (by preference steam heat) is applied thereto until the temperature is raised to 210° F., all the impurities being skimmed off as they rise to the surface. The juice is then boiled until its density (tested by Beaumé's saccharometer) has increased 1° above that previously indicated when the juice was at the same temperature. The source of heat is then removed; and when the temperature of the juice has sunk just below the boiling-point, the subacetate of lead is brought to the consistence of paste by the addition of water, and thoroughly mixed with the juice by stirring. The patentee states that the proportion of salt of lead which he has found to answer is about one-sixth per cent. of the juice.

The second part of the invention consists in using sulphite of lead in the manufacture of a white pigment. When sulphurous acid gas is introduced into saccharine solutions which have been treated with subacetates of lead, it combines with the lead and forms sulphite of lead, which precipitates. The patentee states, that the sulphite of lead may be used with advantage as a paint, instead of white lead; it "covers" well, and does not blacken when exposed to hydrosulphuric acid. It is to be prepared and used in the same manner as white lead. This part of the invention is not confined to the use of sulphite of lead obtained in the manner just described, as sulphite of lead produced in any other way may be employed.—Sealed Feb. 21, 1850.

THE CHEMICAL GAZETTE.

No. CXCI.—October 1, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Volatile Products of Oxidation of Oil of Turpentine by Nitric Acid. *By* Dr. F. C. Schneider.

It was proved, in a former investigation* of the products of oxidation of the oily hydrocarbons obtained in the dry distillation of the fats, that the volatile carbohydracids may be prepared from substances containing no oxygen by a process of oxidation. Gerhardt's discovery of the aldehyde of capric acid in oil of rue justifies the supposition that the hydrocarbons which occur in nature in the form of essential oils may likewise be converted by oxidizing agents into compounds, which either belong to the group of the carbohydracids, or are at least, by their origin, connected with them. The solution of the question, therefore, whether acids of the general formula ($C^{2n}H^{2n}+O^4$) are formed from the hydrocarbons, is of considerable interest. I have therefore subjected the oil of turpentine, one of the most frequent hydrocarbons in nature, and which may be considered as the representative of a large number of essential oils of the composition $C^{10}H^8$, to the oxidizing action of nitric acid, in order to ascertain whether volatile products of oxidation belonging to the class of the fatty acids are not formed in this case.

The oil of turpentine which I employed was purified by distillation over hydrate of potash, then with water, and lastly alone. It exhibited no acid reaction after this treatment; I used ordinary nitric acid for oxidation, once just as it was, and in a second experiment diluted with an equal weight of water. The result was in both cases the same, nor did it make any difference whether the oxidation was carried on slowly at the ordinary summer temperature, or hastened by the application of heat.

The operation is not without its difficulties: the reaction is almost instantaneous, and the gases and vapours liberated, unless they can freely escape, produce a violent explosion, and put a stop to the experiment, or in the most fortunate case a portion of the foaming mass is projected from the apparatus. To ensure success, the apparatus should have the following construction:—A very spacious tubulated retort is placed obliquely, having the neck directed upwards, and connected as air-tight as possible with one, or still better with two Liebig's cooling apparatus; these are lengthened by addi-

* Chem. Gaz., vol. vii. p. 334.

tional glass tubes, so that the neck of the retort is nearly 18 feet long. The last tube terminates in a spacious balloon, which is well cooled. The whole quantity of the oil of turpentine to be oxidized is poured into the retort at once; the nitric acid is added through the tube in very small portions; the first action of the acid upon the oil may be assisted by heat, but as soon as reaction occurs the fire must be removed. Towards the end of the operation, when the reaction proceeds very slowly, artificial heat may again be applied, and the mass then boiled until none or scarcely any red fumes are given off. 1 part of oil requires from 5 to 6 parts of concentrated acid. The oxidation occupies at least twenty-four hours. During the operation the following phænomena occur:—Soon after the addition of the first portion of nitric acid, the layer of oil in contact with it acquires a brown colour; the next portions of acid produce a rustling noise and evolution of heat, the mass boils violently, red fumes are given off, and the sides of the retort become coated with a resinous viscous mass, which subsequently disappears to make room for a tenacious froth. When this disappears, and a further addition of nitric acid produces no perceptible reaction, the disengagement of fumes continues nevertheless for a long time on boiling. As soon as the oxidation is completed the contents of the retort appear homogeneous; but on cooling, a brown-red resinous substance separates, which dissolves but sparingly in water, imparting to it a yellow colour, a bitter taste and an acid reaction. In appearance it resembles that substance which is likewise obtained in the oxidation of the hydrocarbons, furnished by the dry distillation of the fats, and which consists of a mixture of acids and neutral bodies. Taught by experience that a considerable amount of volatile carbohydracids might be extracted from it by distillation with water, I first distilled off two-thirds of the contents of the retort, and then continued the distillation after the addition of water.

The distillate was of a greenish-yellow colour, and slightly turbid, owing to suspended drops of oil; the milkiness disappeared as the quantity of liquid increased. It was saturated with carbonate of potash, the nitre removed by crystallization, and the mother-liquor then decomposed with concentrated sulphuric acid in order to obtain the volatile acids by distillation. This second distillate was somewhat turbid, possessed the odour of acetic acid and rancid butter, and a strong acid reaction.

I neutralized it with carbonate of soda, concentrated it by evaporation, and decomposed the soda salt with nitrate of silver. A very bulky yellowish precipitate fell, which in a short time became black by the separation of silver. On ebullition, the reduction of the oxide of silver was increased. To facilitate the separation of the mixed salts of silver, I boiled the precipitate with less water than required to dissolve it, and preferred to exhaust the residue separately with more water. In this way the less soluble are separated from the more soluble salts, and they are obtained pure by fewer recrystallizations. The solutions on cooling deposited verrucoid masses of crystals, which were collected in the order in which they separated,

and recrystallized separately. I ascertained their composition by the determination of their atomic weights. The following are the results:—

Butyrate of Silver.	Theory.	Found. I.	II.	III.	IV.
Atomic weight	195	195	194	195	196
Per-centage of oxide of silver	59·48	59·80	59·70	59·56	59·07
Metacetonate of Silver.					
Atomic weight	181	180	181	180	181
Per-centage of oxide of silver	64·09	64·22	63·96	64·38	63·89
Metacetonacetate of Silver.					
Atomic weight	174	174·8	174·9	173	
Per-centage of oxide of silver	66·59	66·36	66·33	67·00	
Acetate of Silver.					
Atomic weight	167	166·6	167	167	
Per-centage of oxide of silver	69·16	69·63	69·28	69·33	

I may just observe, that, with the silver salts of the volatile carbohydracids, the next members of the series, as they resemble each other in physical and chemical respects, crystallize out together in such proportions that we are led to regard them as double salts; thus, in the many determinations of the atomic weights which I had to make in order to satisfy myself of the purity of the salts, I obtained, for instance, several times for the oxide of silver the numbers 61·64, 61·67, 61·27, and for the corresponding atomic weight the numbers 187·8, 188 and 189. A double salt of butyric and metacetonic acids would give 61·70 oxide of silver, and the atomic weight 188.

I must also observe, that I never obtained the acetate of silver in needles as usual, but closely resembling in crystalline form the metacetonate of silver, even when I precipitated the silver with sulphuretted hydrogen, and again combined the free acetic acid with the same base. The analysis of the salt thus purified did not however show a different composition.—Liebig's *Annalen*, July 1850.

Note on Dr. Gregory's *Process for preparing pure Chloroform.* *By* Professor Christison.

The process proposed by Dr. Gregory in the May number* of this Journal for preparing a perfectly pure chloroform, has given occasion to various notices in contemporary journals, some of them laudatory, and others the reverse. Among the latter may be mentioned the statement of a late writer in the 'Pharmaceutical Journal,' that chloroform prepared in Edinburgh, avowedly by the process in question, was found in Liverpool to have undergone decomposition, to have become loaded with chlorine, and to be quite unfit for use. In Dr. Gregory's absence on the continent I have felt it to be my duty to make inquiry into the truth of this statement; and the re-

* Page 189 of the present volume.

sult is, that no less than three manufacturers in Edinburgh have tried the process on a considerable scale, and that all have failed to obtain a permanent article. A chloroform of fine quality is obtained in the first instance, but it does not keep many days, and ere long it becomes so loaded with chlorine that its vapour cannot be inhaled.

I have not had time to investigate fully the cause of this unexpected phænomenon, or to ascertain whether it is an inherent fault in the process, or depends rather on some manipulation having been practised, or left out, which Dr. Gregory may have neglected to particularize. But this much seems certain,—1st, that chloroform, purified by one treatment with pure sulphuric acid, free of nitrous acid, keeps perfectly; 2nd, that such chloroform, if left in contact with ordinary sulphuric acid, containing, as it generally does, an impregnation of nitrous acid, will, in less than twenty-four hours, undergo decomposition, and afterwards rapidly evolve chlorine; 3rd, that if a drop or two of nitrous or common nitric acid be added to an ounce of pure sulphuric acid, the decomposition goes on with far greater speed; 4th, that if the sulphuric acid be carefully freed of nitrous acid, so as not to affect solution of green vitriol, no change may occur in the chloroform for an entire week; 5th, but that, nevertheless, even with pure acid, decomposition begins at last, so that in four weeks the odour of chlorine is intolerable. It therefore seems probable that the best chloroform cannot resist the protracted contact of sulphuric acid; and that even the repeated action of that acid, for example when used to effect thorough purification according to the method of Dr. Gregory, produces some change, which, though inappreciable at first, gradually leads to decomposition in the end. Why this happens, whether it always happens, or in what circumstances, are questions which we are not prepared to answer. It is probable, however, that Dr. Gregory will be able ere long to do so satisfactorily, for there is a specimen of chloroform in his laboratory, which was prepared six months ago by his process, and which is still quite unaltered. Meanwhile it is obvious that manufacturers ought not to adopt that process until further explanations shall have been given. It may be added, that the Edinburgh manufacturers have recalled from their customers the chloroform which had been manufactured by the repeated use of sulphuric acid; and that the spurious article is very easily known by the pungency which is added to the purely ætherial odour of the uncontaminated preparation.—*Edinburgh Monthly Journal of Medical Science*, September 1850.

On Stibæthyle. By C. Löwig *and* E. Schweitzer.

A short time ago the authors published an account of the preparation of stibæthyle and of some of its most remarkable characters*. The following are the results of their further inquiries on this subject.

* Page 201 of the present volume.

Boiling-point and Specific Gravity of Stibæthyle and of its Vapour.—For the determination of the boiling-point the authors employed pure stibæthyle, which was brought into a small retort surrounded by an atmosphere of carbonic acid, and rectified by means of a peculiar apparatus. At 302° F. and a barometric pressure of 730 millim., the boiling-point rises quickly to 316°, and remains constant until almost the last drop has passed over, when the thermometer is placed in its vapour. The specific gravity of liquid stibæthyle is 1·3244 at 61°. To determine the specific gravity of the vapour, Dumas' method was used, except that a balloon filled with chloride of æthyle gas was employed for the purpose; it was filled in the following manner:—The balloon was heated to 104°–113° by immersion in hot water, the point then dipped into chloride of æthyle, and the balloon at the same time cooled below 32° by a refrigerating mixture. A considerable quantity of chloride of æthyle was allowed to enter the balloon, when it was again placed in hot water, and the same operation repeated six times before sealing the point. The balloon was now weighed, and after having filed off the point in an atmosphere of carbonic acid, again heated and dipped into stibæthyle, which was likewise surrounded by an atmosphere of carbonic acid. When a sufficient quantity of stibæthyle had passed into the balloon, it was placed in a bath of chloride of zinc, without however removing the point from the carbonic acid gas, and then heated to 356°. To prevent the vapours of the stibæthyle taking fire, carbonic acid was passed into the apparatus in which the point of the balloon terminated as long as the operation lasted. This arrangement has moreover the advantage, that the stibæthyle which escapes as gas is reobtained. When no more gas was obtained, the point was quickly sealed, and the balloon weighed. The specific gravity of the chloride of æthyle gas resulted from the following calculation:—

State of the barometer	733 millims.
Capacity of the balloon	139 cub. cent.
Increase in weight of the balloon after being filled with chloride of æthyle gas at 100°·4	0·442 grm.
Reduction to 32° and 760 millims.	117 cub. cent.
Specific gravity of the chloride of æthyle gas	2·2292
Weight of 1 cub. cent. chloride of æthyle gas	0·00295 gr.
Weight of 117 cub. cent. chloride of æthyle gas	0·3387
Increase in weight of the balloon after being filled with stibæthyle gas	0·442
Weight of the stibæthyle gas	0·7807
Temperature of the balloon filled with stibæthyle gas on being sealed	356°
Residual chlorethyle gas	0
Reduction of the capacity to 32° and 760 millims.	80·8 cub. cent.
Weight of a quart of air	1·2991 gr.
Weight of a quart of stibæthyle gas	9·6621
Specific gravity of stibæthyle gas	7·438

Or—

	Measures.	Spec. grav.
3 atoms of æthyle gas	=6	=12·1110
1 atom of antimony gas	=1	=17·8871
1 atom stibæthyle gas	=4	=29·9981

and $\frac{29{\cdot}9981}{4} = 7{\cdot}499$.

Compounds of Stibæthyle.—Stibæthyle surpasses, in its powers of combination, all hitherto known simple and compound bodies, with the exception of cacodyle and the halogens; it unites at the ordinary temperature with oxygen, sulphur, selenium and the halogens, with considerable evolution of heat, which in the case of oxygen and chlorine even goes so far as to produce ignition. The combinations of the above-mentioned substances agree in every respect with the corresponding potassium compounds, and are easily converted into each other by double decomposition. 1 atom of stibæthyle combines with 2 atoms of oxygen, sulphur, selenium, &c. No higher or lower stages of combination have hitherto been obtained. Under certain circumstances, however, 2 atoms of æthyle separate from the stibæthyle, and a radical, $C^4 H^5 Sb = AeSb$, is formed. This radical, which unites with 5 atoms O, S, Cl, &c., the authors call for distinction æthylestibyle. It differs from stibæthyle principally by the insolubility of its sulphur compounds in water, whilst the sulphuret of stibæthyle is very easily soluble in it. Owing to this, all the compounds which contain but mere traces of æthylestibyle instantly furnish with sulphuretted hydrogen a yellow precipitate of an exceedingly disagreeable odour.

Stibæthyle and Oxygen.—When stibæthyle is discharged through a small aperture into pure oxygen, it instantly takes fire and burns with a dazzling white light. The same also takes place in the atmosphere; but the inflammation only results after a few seconds, a dense white vapour being previously given off. If, on the contrary, the oxidation takes place slowly, there is obtained, as already stated in a former paper, along with the transparent syrupy mass, a white powder insoluble in alcohol, which has been named for the present stibæthylic acid. The composition of this acid is $(C^4 H^5 Sb)O^5$; it is consequently æthylestibylic acid. The syrupy mass consists of $(C^{12} H^{15} Sb)O^2$. The authors call this compound oxide of stibæthyle, and represent it by $StäO^2$. It is difficult to obtain the oxide of stibæthyle pure by direct oxidation, *i. e.* perfectly free from æthylestibylic acid, which is simultaneously formed. It is procured in greatest abundance by allowing a dilute alcoholic solution to evaporate slowly in a loosely covered beaker; in this case but little æthylestibylic acid is formed, whilst it preponderates when the ætherial solution of stibæthyle is evaporated. The residue is treated with æther, which dissolves the oxide of stibæthyle; it however still contains æthylestibylic acid, from which it can only be separated completely by repeated solution in æther and evaporation of

the ætherial solution. The oxide of stibæthyle is pure when its aqueous solution is not coloured or rendered turbid by sulphuretted hydrogen water; if only a trace of æthylestibylic acid is present, the solution is immediately coloured yellow. Under water the oxidation of the stibæthyle is exceedingly slow, on which account it is best kept under a layer of water.

Oxide of stibæthyle is most easily obtained in the purest state from its combination with sulphuric acid; the latter is dissolved in water, mixed with barytic water, filtered from the sulphate of baryta, the solution slowly evaporated on the water-bath, and the residue exhausted with alcohol in which a compound of oxide of stibæthyle with baryta dissolves, which is decomposed by passing carbonic acid into it. It is now filtered from the carbonate of baryta, when pure oxide of stibæthyle is obtained on evaporation of the spirituous solution. It can likewise be prepared in the same manner from the nitrate. When an alcoholic solution of stibæthyle is shaken with an excess of finely-powdered peroxide of mercury, the oxide is quickly reduced, without however any apparent disengagement of heat, and pure oxide of stibæthyle is formed. Sulphuretted hydrogen has not the slightest action upon it.

In its purest state the oxide of stibæthyle forms a tenacious, perfectly limpid and transparent mass, without any trace of crystallization. When left for several days over sulphuric acid under a bell-glass, it becomes tolerably hard, but again softens on the water-bath. It is readily soluble in water and alcohol, and likewise in æther, but in a less degree. The oxide of stibæthyle has a strong bitter taste, which very much resembles that of the sulphate of quinine; it does not appear to be poisonous, for even large quantities of the aqueous solution taken internally did not cause a tendency to vomit. The oxide experiences no alteration by exposure to the air; it is not volatile. When heated in a glass tube sealed at one end, dense white vapours escape, which burn with a bright flame, and a residue is left containing antimony and carbon; however, the greater portion of the antimony is removed in the distillation. Potassium reduces the oxide, on the application of a gentle heat, with separation of stibæthyle. Fuming nitric acid decomposes it, with violent ignition; dilute acid dissolves it without any disengagement of gas. It dissolves in concentrated sulphuric acid without decomposition. When dry muriatic gas is passed over oxide of stibæthyle, chloride of stibæthyle and water are formed, with considerable evolution of heat. Solutions of hydrochloric, hydrobromic and hydriodic acids immediately convert it into the corresponding haloid compound. Sulphuretted hydrogen has no perceptible action upon it; on evaporating the solution of oxide of stibæthyle which has been saturated with the gas, crystals of sulphuret of stibæthyle are obtained.

The composition of the oxide of stibæthyle was found by the analysis of the nitrate and sulphate which are detailed under the respective salts; it consists of—

Carbon	12 =	72	31·04
Hydrogen	15	15	6·46
Antimony	1	129	55·60
Oxygen	2	16	6·90
		232	100·00

The oxide of stibæthyle behaves exactly like an organic base, and furnishes crystalline salts even with the strongest acids, as sulphuric and nitric acids. The authors have hitherto examined but few of the compounds; they all appear to be easily soluble in water; at all events no salt of any other acid produces a precipitate in a solution of the nitrate of the oxide of stibæthyle.

Nitrate of the Oxide of Stibæthyle, $StäO^2+2NO^5$.—This salt is obtained either directly, by saturating dilute nitric acid with oxide of stibæthyle, or by dissolving stibæthyle in dilute nitric acid. The stibæthyle dissolves just like a metal in the moderately hot acid, with a constant disengagement of bubbles of nitric oxide; at the same time, however, even when very dilute acid is employed, a small quantity of oxide of antimony always separates, which must be removed by filtering the solution. As the nitrate of the oxide of stibæthyle is scarcely soluble in excess of nitric acid, the salt can easily be obtained in crystals from the acid liquid by slow evaporation. When the acid solution is strongly concentrated upon the water-bath, the compound separates in oily drops, which collect at the bottom of the vessel, and solidify to a crystalline mass on cooling. The salt, freed from the acid mother-liquor, is dissolved in a little water, and the solution left to spontaneous evaporation.

The salt forms remarkably beautiful, large, rhomboidal crystals, which are easily soluble in water, less so in alcohol, and scarcely soluble in æther. The solution exerts an acid reaction upon litmus-paper, and possesses the same bitter taste as the oxide of stibæthyle, which indeed is characteristic of all the compounds of stibæthyle. At 144° F. the salt melts to a colourless liquid, which solidifies at 135° to a dazzling white crystalline mass. It deflagrates when heated, like a mixture of a nitrate with carbon. Concentrated sulphuric acid immediately separates the nitric acid; and if an aqueous solution of the salt is mixed with strong muriatic acid, chloride of stibæthyle is obtained as a colourless oily liquid. Sulphuretted hydrogen has no action upon the compound.

The salt was burned with oxide of copper mixed with metallic copper. To estimate the nitric acid, the aqueous solution of the salt was mixed with barytic water, and evaporated to dryness on the water-bath. The residue was mixed with absolute alcohol, and the compound of oxide of stibæthyle with baryta decomposed by a current of carbonic acid; the whole was then brought upon a filter, the residue washed once or twice with alcohol, then treated with water, and the baryta in the filtered solution precipitated by sulphuric acid. Analyses:—

Carbon	22·26	21·60	..	12 =	72	21·40
Hydrogen	4·55	4·62	4·62	15	15	4·41
Antimony	..	..	..	1	129	37·94
Oxygen	..	..	..	2	16	4·87
Nitric acid	32·20	..	..	2	108	31·78
					340	100·00

As the nitric compound is easily obtained in a perfectly pure state, it is better adapted than any other for the preparation, especially of the haloid compounds of stibæthyle.

Sulphate of the Oxide of Stibæthyle, $StäO^2 + 2SO^3$.—This compound may likewise be prepared in a direct manner, but it is obtained most pure by the exact decomposition of the sulphuret of stibæthyle by sulphate of copper; aqueous solutions are employed. The sulphate is exceedingly soluble in water, and consequently crystallizes only from the syrupy liquid in small perfectly white crystals. An excess of sulphuric acid prevents the crystallization, but it has no decomposing influence upon the oxide of stibæthyle. The crystals are pressed between paper, and then dried over sulphuric acid. They experience no loss at 212°, but become soft and melt at a somewhat higher temperature to a colourless liquid. This salt also possesses a bitter taste, is void of smell, pretty easily soluble in alcohol, but almost insoluble in æther. Muriatic acid immediately separates chloride of stibæthyle from the aqueous solution.

To estimate the sulphuric acid, the salt was dissolved in water and the solution precipitated with nitrate of baryta; if chloride of barium is used, the sulphate of baryta must be washed several times in alcohol in order to remove the adherent chloride of stibæthyle. 24·45 and 25·58 per cent. of sulphuric acid were found; theory requires—

Carbon	12 =	72	23·08
Hydrogen	15	15	4·80
Antimony	1	129	41·03
Oxygen	2	16	5·46
Sulphuric acid	2	80	25·63
		312	100·00

[To be continued.]

On the Constitution of Apiine.

By Dr. von Planta *and* W. Wallace.

The authors prepared the apiine by exhausting fresh parsley several times with boiling water, straining the liquid through linen, and drying on the water-bath the gelatinous mass which separates on cooling. In this manner a dirty green powder was obtained, which was repeatedly exhausted with boiling alcohol. The filtered solution solidified on cooling to a jelly, the alcohol was removed by distillation, and the sediment collected on linen. After pressure the substance was of a greenish-white colour. It was now repeatedly moistened with hot alcohol, and again pressed, and the

residue treated with æther so long as it removed anything. The substance thus purified the authors call apiine. In the expressed alcoholic liquids there is still some apiine contained, which may be separated by distilling off the alcohol and digesting the residue with æther. A dark green solution is obtained, which leaves, on evaporation of the æther, a green varnish consisting of chlorophylle and a waxy body. On boiling the varnish with water, the green wax melts, and subsequently congeals to a brittle shining mass, which melts at 140°, and is only saponified with difficulty by boiling with caustic potash.

Apicine, $C^{24}H^{14}O^{13}$, forms a soft colourless powder, void of taste and smell. After being dried over sulphuric acid, it lost at 212° 4·21 per cent. of water, and reabsorbed the same amount on being subsequently exposed to the air. Its weight is not altered by being heated from 212° to 356° F.; at the latter temperature it melts very uniformly and very quickly to a mass, which on cooling is yellowish, brittle, and of a vitreous lustre. Between 392° and 410° it begins to be decomposed. When carefully melted apiine is mixed with boiling water, it dissolves far more readily than previous to fusion, and solidifies on cooling to a transparent firm jelly; it consequently undergoes not the slightest change either in its composition or in its properties by fusion. It melts very readily upon platinum foil, takes fire, puffs up, and becomes carbonized. It still left 0·15 per cent. of ash. Apiine is very insoluble in cold water; 1 part requires 8500 parts of water; but it is very readily soluble in boiling water. 1 part of apiine dissolved in 1537 parts of boiling water still formed on cooling a loose gelatine. It dissolves in 389 parts of cold alcohol, but far more readily in boiling alcohol. When the alcoholic solution is not too dilute, the apiine gelatinizes from the yellowish solution on cooling in the same manner as from the aqueous solution.

Protosulphate of iron strikes a blood-red colour with solutions of apiine, which in the case of pure apiine disappears only with a dilution of 8500 times. It had already been stated by Braconnot, that 1 centigrm. of apiine, dissolved in boiling water, and then diluted with 20 quarts, furnished a liquid, which, on the addition of 1 centigrm. of protosulphate of iron, still had a reddish appearance. Neither chloride of barium, acetate of lead nor nitrate of silver produced precipitates in the hot aqueous or alcoholic solutions of the apiine; an alcoholic solution of lead strikes an intense yellow colour with an alcoholic solution of apiine.

Apiine does not form any constant compound with the metallic oxides, and the precipitates which salts of lead produce in its solution furnished a varying amount of lead; at one time 53·60 per cent. of oxide of lead was obtained, at another time 61·09. The analyses of apiine of different preparations gave—

Carbon	55·25	55·05	54·71	24	=144	54·96
Hydrogen	5·59	5·49	5·60	14	14	5·34
Oxygen	39·16	39·46	39·69	13	104	39·70

Alteration of Apiine by boiling Water.—By long ebullition with water, apiine absorbs 2 atoms of water and loses its property of gelatinizing. The altered apiine is brittle, and easily reduced to a powder, which is of a brown colour. It dissolves readily in boiling water, but does not gelatinize on cooling. Heated upon platinum, it does not melt like pure apiine previous to its decomposition. Both the alcoholic and the hot aqueous solutions are coloured blood-red upon the addition of protosulphate of iron. Chloride of barium causes a slight turbidness in the hot aqueous solution; acetate of lead a copious precipitate, which does not disappear on ebullition. Nitrate of silver is without effect. The analysis of the modified apiine, which after treatment with boiling water had separated as a light, flocculent, almost colourless precipitate, gave—

Carbon	50·98	24 =	144	51·43
Hydrogen	6·03	16	16	5·71
Oxygen	43·09	15	120	42·86

Apiine and dilute Mineral Acids.—When apiine is dissolved by heat in dilute sulphuric acid, and the solution then boiled for twenty minutes or longer, it is converted into a substance which contains 4 atoms less water than apiine. This substance is deposited on the cooling of the solution as a whitish flocculent precipitate, which shrinks considerably upon the filter. Carefully pressed between blotting-paper, dried over sulphuric acid, and then in the water-bath, and reduced to powder, this substance has a pale brown colour. The same body was always obtained whether the ebullition was carried on for half an hour or for a whole day. It is also formed when the water contains only 1 per cent. of sulphuric acid. In the same volume of boiling water in which apiine dissolved with ease, this substance modified by acids is almost insoluble, and even in twelve times the amount very little of the brown powder dissolves. The soluble portion separates on cooling in the form of white flakes, the quantity of which is in proportion to the amount of water used and the length of the ebullition.

It dissolves however readily in boiling alcohol, but does not separate again on cooling even after long standing. Both solutions have a neutral reaction, and protosulphate of iron produces in them, either hot or cold, a reddish-brown flocculent precipitate. Chloride of barium, acetate of lead and nitrate of silver have no effect. It differs also in its deportment at a high temperature from apiine, melting at a much higher temperature, and then not without decomposition. This substance gave on analysis—

Carbon	63·67	63·34	63·45	24 =	144	63·71
Hydrogen	4·41	4·56	4·53	10	10	4·42
Oxygen	31·92	32·10	32·02	9	72	31·87

Apiine does not yield any sugar by ebullition with dilute sulphuric acid.

Apiine furnishes, after half an hour's ebullition with dilute muriatic acid, a substance which has the same composition as, but other properties from that prepared by means of sulphuric acid.

When the dilute acid is poured over it, the apiine assumes a yellow colour, which the solution retains; but on boiling, it soon becomes turbid, and deposits a whitish flocculent precipitate, which is not dissolved by continued boiling. It retains upon the filter a looser form, and does not shrink so much; the dry powder is light brown. This body is far more soluble in water than that obtained under the same circumstances with sulphuric acid. The solution in boiling water has a yellowish colour, does not gelatinize on cooling, but appears colourless after the separation of a copious precipitate; it is readily soluble in boiling alcohol, and continues in solution like that obtained with sulphuric acid after long standing, without the separation of any precipitate. The aqueous and alcoholic solutions strike a brick-red colour with protosulphate of iron, and deposit a reddish-brown precipitate; the precipitate is not dissolved by boiling nor the liquid decolorized. Acetate of lead produces in the hot aqueous solution a slight precipitate; chloride of barium and nitrate of silver are without effect. This substance furnished on analysis—

Carbon	64·36	24 =	144	63·71
Hydrogen	4·54	10	10	4·42
Oxygen	31·11	9	72	31·87

Concentrated Mineral Acids and Apiine.—Apiine dissolves in concentrated muriatic or sulphuric acid without the application of heat. Water precipitates from the solution a flocculent yellowish substance, which when reduced to powder is yellowish-brown. It contains 2 atoms less water than apiine. When heated, the apiine is blackened by sulphuric acid with evolution of sulphurous acid, and the clear solution which it forms with concentrated muriatic acid soon becomes turbid, and deposits a copious dark brown flocculent precipitate. The analysis of the substance, precipitated by water from the cold solution in sulphuric or muriatic acid, gave—

Carbon	59·06	24 =	144	59·01
Hydrogen	5·08	12	12	4·91
Oxygen	35·86	11	88	36·08

Apiine and Alkalies.—Apiine dissolves readily in potash or ammonia, and acids precipitate it from the solution in a gelatinous and unaltered state. The solution in dilute caustic potash was orange-red. The substance precipitated by means of an acid from the solution had the same composition as apiine, viz.

Carbon	54·87	24 =	144	54·96
Hydrogen	5·73	14	14	5·34
Oxygen	39·40	13	104	39·07

Apiine and Chlorine.—When chlorine is passed into a hot aqueous solution of apiine, a dirty yellow precipitate containing chlorine is obtained. Its solution in hot alcohol or water is neutral; the latter on cooling deposits a flocculent yellowish precipitate. The hot aqueous solution strikes a blood-red colour with protosulphate of iron, which does not disappear on ebullition. Acetate of lead produces in the hot aqueous solution a copious yellow flocculent precipitate, which is not dissolved by boiling.

Apiine and Muriatic Acid Gas.—When apiine is exposed to a current of dry muriatic gas at 212°, it acquires a yellow colour, which again disappears on the application of heat; in two experiments it had increased 5·111 and 5·132 in weight.

Apiine and Nitric Acid.—According to Braconnot, apiine yields nitropicric and oxalic acids with nitric acid. The authors found this statement to be correct with respect to impure apiine, but not so with the pure substance.

Apiine furnishes, on distillation with manganese and sulphuric acid, carbonic, formic and acetic acids.—Liebig's *Annalen*, lxxiv. p. 262.

ANALYTICAL CHEMISTRY.

Observations on Boracic Acid and its Quantitative Determination. *By* Prof. H. Rose.

It is well known that various difficulties are met with in the estimation of boracic acid, which as yet have not been entirely overcome by the methods recommended. When the boracic acid is dissolved in water, its entire amount cannot be obtained by evaporation. When moreover the acid obtained by evaporation from its aqueous solution is heated to fusion in a platinum crucible, its weight continually decreases unless access of air be most carefully prevented. The decrease in weight becomes far more considerable when the temperature is raised to a strong red heat. This loss however amounts only to a few milligrammes, unless the heating occurs in a moist atmosphere. But if the cooled boracic acid is moistened with a drop of water and again heated to redness, the loss in weight amounts to some centigrammes, and it becomes much more considerable when a drop of alcohol is used instead of water. The loss in weight which occurs on melting boracic acid is best avoided by placing a small quantity of carbonate of ammonia upon the surface of the acid.

It has been proposed to prevent the volatilization of the boracic acid on evaporating its aqueous solution by supersaturating it previously with ammonia. But the affinity of boracic acid for ammonia is so slight that the latter is expelled with the aqueous vapour.

Even the addition of chloride of ammonium to an aqueous solution of boracic acid does not prevent the volatilization. On evaporating the whole, after the addition of this salt, and heating the dry residue in a platinum crucible until no more fumes of chloride of ammonium are liberated, a residue is obtained which cannot be fused at the temperature at which pure boracic acid readily melts. On treatment with water, nitruret of boron is left undissolved in the form of a whitish-gray powder; its quantity varies, and sometimes not even a trace is produced.

It is likewise impossible to determine the boracic acid quantita-

tively in its aqueous solution, in a similar manner to arsenic and phosphoric acid, by adding to the solution a weighed quantity of recently-calcined oxide of lead, evaporating the whole, and heating or igniting the dry mass; for it is not possible to prevent the escape of boracic acid on evaporation by the addition of oxide of lead. Nitrate of lead is as useless for the purpose as the pure oxide.

No quantitative result can be obtained even by the addition of a weighed quantity of tribasic phosphate of soda, $3NaO, PO^5$, for this salt does not prevent the volatilization of the boracic acid from its aqueous solution.

In fact, it is only possible to estimate quantitatively the boracic acid in its aqueous solution by the addition of a weighed quantity of a fixed alkaline carbonate. But this method is somewhat tedious, and requires much time and attention. Carbonate of soda is preferable to the carbonate of potash, as it can be more readily weighed off with accuracy. It is weighed off in the fused state, and about the same or twice the quantity of it taken to the amount of boracic acid supposed to be present in the solution. It is dissolved in the solution, and the whole evaporated at a gentle heat. At the ordinary temperature carbonic acid is not expelled from the carbonated alkalies by the free boracic acid; and at a higher temperature, as also on evaporation only in a very slight degree; it is only after the whole has been evaporated to dryness, and the dry mass is strongly heated, that any evolution of carbonic acid takes place, when it is necessary to be particularly careful. With a strong heat the mixture is liquid, but at a fainter heat only tenacious. If it be fused at as high a temperature as it is possible to produce with a spirit-lamp and a double draft, a constant weight is obtained on cooling, which does not vary even after long standing. But if the crucible is exposed to a moderate heat, after having been previously exposed to a strong red heat, it curiously enough increases in weight, and it is not possible to obtain by this means a constant weight. The result moreover is the same whether the fusion of the mass has been continued for a longer or shorter time, and whether a higher or lower temperature has been employed. The carbonic acid in the fused mass is now estimated. If we subtract from the weight of the fused mass the amount of soda in the carbonate of soda employed, and that of the carbonic acid which has escaped during the experiment, we obtain the quantity of boracic acid with great accuracy. The same phænomena occur with the employment of carbonate of potash, but the results are somewhat less accurate, as this salt cannot be weighed off so carefully in the anhydrous state as the carbonate of soda.

This method of estimating the amount of boracic acid in its aqueous solution can however be rarely employed, and only when the solution contains no other substance than perhaps ammonia, which is expelled even without the action of carbonate of soda.

The best and most accurate method of separating boracic acid from bases is, as is well known, that by means of hydrofluoric and sulphuric acids, when the boracic acid is expelled as fluoride of

boron, and the bases are obtained in the state of sulphates. But boracic acid may likewise be entirely expelled as boracic æther by treating the borates with sulphuric acid and alcohol. This method however is far less accurate than that by means of hydrofluoric acid, and should only be employed when concentrated hydrofluoric acid cannot be procured. When hydrochloric acid is used instead of the sulphuric acid, as proposed long ago by C. Gmelin, the boracic æther is far less easily produced, and the volatilization of the boracic acid proceeds very slowly and is not so complete.

Since boracic acid does not form with any base a compound which is entirely insoluble in water, no direct method of estimating this acid is as yet known. The only compound by means of which it might be completely separated is the fluoboride of potassium; this salt is very sparingly soluble, and resembles the silicofluoride of potassium, and like it is insoluble in alcohol. Berzelius states that it is somewhat soluble in it, which however is not the case. But it is more soluble in a solution of chloride of ammonium than in pure water. A large number of experiments however have shown that it is not possible to separate boracic acid quantitively as fluoboride of potassium; it does not even succeed when free boracic acid is contained in the solution. When pure hydrofluoric acid is added to the solution, and then carbonate of lime to separate the excess of acid, and lastly acetate of potash and alcohol to the filtered liquid, a fluoboride of potassium is obtained, which always contains fluoboride of calcium. But when the boracic acid is combined with a base, for instance with soda, and the above plan is adopted, the results are far less accurate. With regard to the separation of boracic acid from phosphoric acid, Von Kobel has proposed to effect it by adding to both solutions one of perchloride of iron, and precipitating the whole by an excess of carbonate of lime. The addition of the solution of perchloride of iron is however not necessary. When hydrochloric acid is added to the solution of a borate, and the whole is treated in the cold with an excess of carbonate of baryta, no boracic acid is contained in the insoluble residue, which consists solely of carbonate of baryta. Phosphoric acid, on the contrary, both in the free and combined state, is entirely precipitated in the cold by carbonate of baryta, when some nitric or hydrochloric acid is added to the solution. Boracic acid can therefore be separated from phosphoric acid by carbonate of baryta. The greatest accuracy however is not attained by it, as the phosphate of baryta is not perfectly insoluble in a solution of borax. When phosphate of baryta is digested in the cold with a concentrated solution of borax, the filtered solution contains after a time traces both of baryta and phosphoric acid, which latter is readily detected by molybdate of ammonia. When therefore a mixture of phosphate and borate, after the addition of hydrochloric acid, is treated in the cold with an excess of carbonate of baryta, frequently stirred and filtered, after twenty-four hours the wash-water leaves, even after long edulcoration, a residue on evaporation, and shows with molybdate of ammonia traces of phosphoric acid. But if the

insoluble residue, after having been washed for a time, is dissolved in hydrochloric acid, the baryta removed by dilute sulphuric acid, the phosphoric acid precipitated as ammonio-phosphate of magnesia, and the amount of phosphoric acid calculated from the calcined residue, a loss of phosphoric acid is found, but it is not considerable; so that a result approaching very closely to the truth may be obtained according to this method.

When ammonio-phosphate of magnesia is digested in the cold with a concentrated solution of borax, no phosphoric acid can be detected in the filtered solution. From a solution containing boracic and phosphoric acids, the latter may consequently be separated by precipitating it as ammonio-phosphate of magnesia, unless the solution contain at the same time other substances, which are precipitated on the addition of ammonia and a solution of magnesia. The precipitate contains a very slight trace of boracic acid. A small excess of phosphoric acid is therefore obtained according to this method, which is about as great as the loss which occurs with the method by carbonate of baryta.

The difficulties attending the estimation of fluorine in the presence of boracic acid have not yet been overcome. If the solution be acidified with nitric acid, an excess of carbonate of lime added, and the whole heated and filtered, the insoluble portion does not contain the whole amount of the fluoride of calcium corresponding to the fluorine in the solution. Fluoborides have been formed, which are not at all, or only partially decomposed by treatment with carbonate of lime.

Boracic acid can be entirely separated from bases in insoluble compounds by fusion with an excess of carbonated alkali. At least on fusing borate of baryta and borate of magnesia with carbonate of soda, and treating the fused mass with water, the total amount of the bases was obtained perfectly free from boracic acid.—*Berlin. Berichten*, 1850, p. 201.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a Method of fixing Colours upon Tissues. *By* C. Broquette.

When an egg is boiled in a colour-bath, the colour immediately fixes itself to the shell. Egg-shells contain, like bones, an organic tissue and mineral salts. If it is attempted to dye these mineral salts, —the phosphate or carbonate of lime—separately, it fails, and therefore neither of these salts can be regarded as the mordant. If, on the contrary, it is attempted to colour the organic tissue of egg-shells or of bones, this immediately becomes dyed; hence it follows that the organic matter of the bones and egg-shells is the mordant.

Now in the same manner as mineral mordants have hitherto been employed to fix colouring matters upon cotton, organic mordants

may be used, and Broquette has already employed caseine for this purpose. The coating of vegetable fibres with animal substances was first carried out by M. Hausmann, as observed by M. Barreswil, in this article, but is said never to have attained to any importance. The caseine must of course be first dissolved, in order that the tissues may be permeated by the solution, but it must then be rendered insoluble in the tissues. Now it has been shown by Braconnot that caseine furnishes a soluble compound with ammonia, which is again decomposed by boiling. Broquette therefore impregnates the goods with a solution of caseine in ammonia, then heats them to expel the ammonia, upon which the caseine remains in an insoluble state in the tissues.

Cotton goods, after this treatment, are saturated with animal matter, and may now be dyed in the same colour-baths as those used for woollen tissues.

Frequently the dyes are alkaline; they then dissolve the caseine, instead of being fixed by it. But since Bachelier used as a cement a mixture of lime and caseine, it is known that this mixture hardens and becomes fixed. Broquette therefore employs the caseine sometimes with lime alone, sometimes with ammonia and lime together, and saturates the goods with this caseate of lime, which soon sets in a warm atmosphere, and then resists the alkalies and rinsing with alkaline liquids.

By this treatment, the cotton acquires a peculiar stiffness; so that although its capacity for dyes has become nearly equal to that of wool, it is far behind the latter owing to want of lustre. But this evil can also be remedied by mixing the mordant with oil. Oil, caseine and lime form a mordant which fixes the colours with a perfectly remarkable lustre.

When the goods to be dyed consist of wool and cotton, a different plan has to be followed; the mordant in this case is not adapted for the two materials; the wool is deprived of its natural lustre and the cotton tissues are not sufficiently penetrated. For such goods Broquette employs the mordant before the weaving; it is applied to the cotton in the spinning, when it can afterwards be woven and bleached like wool, without the mordant experiencing any injury. When threads thus prepared are woven, the tissues can be dyed just like woollen stuffs without further treatment.

By means of the solution of caseate of lime, mineral colours which are insoluble in water can be adapted to the dyeing of stuffs; they are mixed in a state of very fine powder with the solution. These liquid colours, which can be prepared for instance with ultramarine, ochre, &c., can again be removed with water, unless they have been dried; but as soon as they coagulate, they adhere firmly to the tissues inclosing the colouring principle.

A further application of the mordant of caseine, oil and lime is in the printing of stuffs; in this case we are not limited merely to mineral colours, which by its aid may be fixed upon the goods, but the numerous vegetable colours may be likewise very well applied, by first converting them into lakes by means of alumina or prot-

oxide of tin, and then using these lakes in the same manner as the powdered mineral colours. After being printed, the goods are wrapped in moist linen, and left for about half an hour in the moist vapour in a warm atmosphere. During this time the impressed colour does not dry superficially, but is absorbed into the interior of the fibres, and is then completely fixed in the subsequent drying.

This new method of mordanting has already had considerable influence upon several pigments, for instance upon archil, which has only been used for dyeing exceptionally; according to Broquette's process, some very beautiful colours are obtained from it, modifications of the peculiar colour of the archil by lime.

It will be evident, from what has been above stated, that in this process of dyeing it is requisite to pass the goods through a lime-bath, which will not do for many dyes, as the colours have their tints altered by such treatment. In such cases magnesia is to be substituted for the lime.

When goods are printed with the mineral colours or lakes, according to the above process, very full colours are obtained, which in the case of many patterns is not desirable. To bring out the shades and half-colours in the full-coloured impressions, the printed goods are placed with their coloured surface upon an absorbing ground, cotton stuff, and the forms pressed on the back. The printed portion pressed upon the absorbing surface is deprived of some of its colour, and numerous patterns can be produced in this manner.—*Journ. de Chim. et de Pharm.*, xvii. p. 271.

On the Refining of Gold. *By* Dr. Philipp.

The process of refining gold by the dry method, called the process of cementation, has been long known, although it has sometimes been considered a secret, and is employed but by very few persons for refining alloyed gold, its use being principally to remove from that metal bodies which form an obstacle to its malleability. Experiments have been made for completely refining gold by way of cementation; but, in operating thus, loss of the precious metal has been observed on the one hand, and on the other sufficient purity has not been obtained; the consequence of which is that the old processes have been retained. After numerous experiments, M. Philipp has arrived at the conclusion, that, by means of cementation, gold may be obtained of the greatest possible purity, that is to say, of the quality known in commerce as fine gold. The success of this very simple operation depends,—1st, upon the choice of the ingredients used for cementation; 2nd, upon the preparation of the mass; 3rd, upon the degree of fineness of the alloy to be treated; and 4th, upon the temperature employed.

1. *Ingredients employed for Cementation.*—Many receipts have been proposed for this purpose. Thus, to refine 1 grm. of gold, the following ingredients have been employed, viz. 6 grms. of brick-

dust, 2 grms. of protosulphate of iron, ½ grm. of alum, 2 grms. sea-salt, 1 grm. saltpetre, ½ grm. sal-ammoniac, or 12 grms. of brick-dust, 6 grms. of sea-salt, 3 grms. of sulphate of zinc, ¾ grm. saltpetre, or 6 grms. brick-dust, 1½ grm. sal-ammoniac, ¾ grm. sea-salt and ½ grm. carbonate of soda. These receipts did not furnish satisfactory results. In fact, the two first occasion a loss of gold (as the saltpetre and sea-salt should not be employed together), and the latter furnishes gold which contains silver.

The following formula is at once more simple and more advantageous, viz. 3 grms. brick-dust, 1 grm. sea-salt, 1 grm. alum and 1 grm. sulphate of iron.

2. *Preparation of the Mass.*—The sea-salt, alum and sulphate of iron, after being thoroughly dried, are reduced to fine powder, which is added to the brick-dust, and mixed intimately until the whole becomes one homogeneous mass. This powder is then damped with a little wine-vinegar, to form a paste, in the midst of which the gold to be operated upon is placed, and the whole is introduced into an earthen vessel or melting-pot. When the gold is in fragments, it may be distributed throughout the mass.

3. *Quality of the Gold.*—Gold of from 8 to 12 carats is the best adapted for this method of refining. With finer gold, the matters which dissolve the alloyed portions cannot so readily penetrate the mass, as it is not sufficiently porous. If therefore the gold is finer, it must be alloyed with copper until it is of the desired quality. With gold of less than 8 carats, there is, on the other hand, this inconvenience,—that the mass of gold which remains after the operation does not possess sufficient consistency to allow of its being extracted without loss from the powder of cementation.

4. *Temperature employed in the Operation.*—The melting-pot or vessel is introduced into a charcoal fire, covered up, and heated slowly, so as not to become red-hot in less than three or four hours. The duration is regulated according to the thickness of the gold, being less for laminated gold and thin leaf-gold. A dull red heat appears to be the most advantageous; for, if at the commencement, or during the course of the operation, too great a heat be applied, the decomposition of the materials will be too rapid, and the products will not act sufficiently upon the gold. When the crucible is cold, the powder adhering to the gold is carefully detached and completely removed by means of boiling water. The gold in this state is porous and friable, and of a fine pure yellow colour. It is fused into a mass with borax.

The following is the explanation of the operation:—In the presence of the sulphuric acid of the sulphate of iron the sea-salt gives off chlorine, which converts the gold into chloride; but, at the temperature indicated, it is reduced to the metallic state, whilst the other metals originally mixed therewith are dissolved in the powder of cementation. The alum delays the operation, and the brick-dust, by its interposition, favours the slow and gradual disengagement of the chlorine.—Newton's *Journal*, August 1850.

On the Bronzing of Plaster Figures. By M. L. Elsner.

The following receipt was given, some time since, in a scientific journal, for bronzing plaster figures:—"Dissolve 500 parts of white soap in water, and add thereto 150 parts of sulphate of copper; a green precipitate is thus formed, which wash and dry, and redissolve in essence of turpentine, or other siccative essence; with this solution coat the figures required to be bronzed (having previously heated them), and when dry they will possess a fine bronze colour."

M. Elsner states, that, by following the above directions, a good imitation of bronze is not obtained, as the preparation acquires a grass-green colour, and has not the tone of bronze. On the other hand, a brownish-green bronze may be very easily obtained by adding to a solution in water of palm-oil soap a mixture of sulphate of iron and sulphate of copper in solution; this furnishes a brownish-green precipitate, the colour of which may be modified at pleasure by the addition of a greater or less quantity of one or other of these salts. The precipitate, after being washed and dried, is redissolved in a siccative essence, or a mixture of good varnish of linseed oil and wax; and with this solution the figures (having been previously heated) are coated; on drying, they will be found to possess a brownish-green bronze colour.

The yellow principle, obtained in a solution of palm-oil soap by means of a solution of sulphate of iron, is palmitate of iron, as the palm-oil soap may be considered to consist in great part of palmitate of soda. Palmitate of copper has a grass-green colour. These two metallic soaps are both soluble (without losing their colour), by the help of heat, in essence of turpentine and fatty oils.

A soap, for obtaining this bronze colour, may also be prepared with linseed oil and caustic soda lye, treating the liquor with a solution of a mixture of sulphate of iron and sulphate of copper, and treating the precipitate formed as above. Palm-oil soap, which is to be met with in commerce, seems however much better adapted for the purpose.

Plaster figures may also be covered with a brownish-yellow bronze by laying over them a coating of mosaic gold (bisulphuret of tin) and linseed-oil varnish.

M. Elsner states, that he has succeeded in obtaining a much better result by employing a solution of the salt of iron only, instead of a mixed solution of the sulphates of iron and copper, for forming a precipitate from the soapy solution, as by that means a soap of definite composition is obtained, and consequently a determinate brown-yellow colour. On afterwards dissolving the metallic soaps separately by means of heat in a fatty medium, and pouring one solution into the other, the shade required for imitating bronze may easily be determined.—*Newton's Journal*, Sept. 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Luminosity of Phosphorus. *By* Prof. R. F. MARCHAND.

THE luminosity of phosphorus is usually ascribed to an oxidation of its vapour, a view which Fischer has recently endeavoured to support by his experiments; or it is considered, with Berzelius, to result from evaporation, and the molecular change thus produced. A third view is that of Schönbein, who ascribes the luminosity of phosphorus rather to the influence of ozone than to that of the air. Schönbein also states, that phosphorus is neither luminous nor forms any ozone in pure moist or dry oxygen, and that those substances which prevent the luminosity of phosphorus are those which combine with ozone or decompose it. Lastly, the gases in which phosphorus is luminous, and the substances which prevent the luminosity, have been made known by the experiments of Graham.

In contradiction to many of the statements hitherto published, Marchand has found by his experiments, that, in accordance with the view of Berzelius, phosphorus is luminous in all gases and all vapours, and that this is not the case only when the substances which form the atmosphere around the phosphorus, or are mixed with it, unite chemically with the phosphorus. With many gases the temperature may be very low, while with many vapours it must attain nearly the boiling-point of phosphorus.

According to Marchand, the luminosity is owing to the evaporation of the phosphorus and to a simultaneous or previous molecular change; it differs from the luminosity which occurs in oxidation, and both can be produced separately. The luminosity continues as long as the phosphorus can evaporate in the slightest degree, and at such a low temperature that it has lost nearly all tension. It ceases when it has become covered with a coating which hinders the evaporation. At 5° F. the evaporation of the phosphorus is immeasurably small, but the luminosity is nevertheless not quite suspended.

The manner in which these experiments were made differs from those followed by other chemists, inasmuch as the phosphorus was allowed to evaporate, not in closed spaces filled with gas, but in a current of gas.

Experiment in Hydrogen.—The disengagement apparatus was in the form of a very large Döbereiner's light machine, and the air had been completely expelled by the disengagement of gas for several

weeks previously. The gas passed first over a layer of incandescent platinum sponge, and then through a chloride of calcium tube, and was employed in a perfectly pure and dry state. The phosphorus over which this gas was passed was contained in a glass tube drawn out anteriorly. In the dark the piece of phosphorus appeared luminous at its surface, and gave off a luminous atmosphere, which was carried some distance with the hydrogen gas. The experiment, which was carried on uninterruptedly for more than eight days, underwent not the slightest change during this time. The piece of phosphorus protected from the light retained its vitreous appearance. A strip of paper, coated with iodide of potassium paste, and inserted in the front of the tube, remained perfectly colourless the whole time it was kept there, although the hydrogen, when ignited on its exit from the tube, exhibited a beautiful green cone in the flame, caused by the phosphorus vapour carried away; consequently no formation of ozone had taken place. When the current was increased, the brilliancy of the piece of phosphorus was heightened, and the luminous cloud was blown forward, passed through the whole length of the glass tube, and came out at the point, whilst the interior of the tube remained dark until the current was again weakened.

This phænomenon can be explained only on the assumption that a certain amount of phosphorous vapour is requisite to produce the luminosity. The cause cannot be found in a cooling of the phosphorus by increased evaporation in the stronger current of gas, since the luminosity can be produced even at 5°. For instance, some phosphorus was placed in a U-shaped tube, and this cooled to −7°·6 F. At this temperature the phosphorus gave off no light in the current of hydrogen; but when the temperature had risen again to 5°, the phosphorus diffused a very distinct light for hours, of slight intensity it is true, and without forming any perceptible cloud; but on increasing the current, the warmer portion of the glass tube projecting out of the refrigerating mixture became luminous; and the light of the piece of phosphorus itself was extinguished even with a less current than at the ordinary temperature of 59° to 64°. When the open end of the U-shaped tube was closed, the luminous cloud sank into the cold portion, the piece of phosphorus itself became luminous, and remained so for a long time. It is however probable that the temperature of 5° is not the lowest at which phosphorus continues to give off light.

Experiment with Carbonic Acid.—On employing pure carbonic acid, the results of the experiment were the same.

These phænomena cannot be explained by an oxidation, as it was impossible for the phosphorus in both these cases to become in the least oxidized. Litmus-paper remained perfectly unchanged in the effluent gas. If some chemists have found that phosphorus only continued to diffuse a light for a certain time in hydrogen, this must be owing to their having made the experiment in a confined space, which soon became filled with the vapours of phosphorus, whereby the evaporation of the phosphorus was prevented. For the same

reason phosphorus is only luminous for a short time in a Torricellian vacuum.

That phosphorus ceases to be luminous in compressed air has long been known from the experiments of Hellwig; Davy determined the requisite pressure to be 4 atmospheres. Marchand found that a pressure of 2 atmospheres at 5° destroyed the luminosity of the phosphorus in dry gases. On subsequently removing the pressure, the piece of phosphorus, and the entire tube in which the compression of the gas was effected, is filled with a luminous vapour, which soon disappears, whilst the phosphorus continues to give light.

Naphtha, oil of turpentine and sulphuretted hydrogen prevent the luminosity of the phosphorus, but their action can be neutralized by a higher tension of the phosphorus. The extinguishing power of the vapour of æther can easily be shown by holding an open glass in which some fragments of phosphorus are contained beneath a watch-glass, into which a few drops of æther have been poured. The vapour of the æther sinks down to the bottom of the glass and the light instantly disappears. When phosphorus is heated in a current of hydrogen charged with the vapour of æther, it begins to give light far below its boiling-point; the whole tube is filled with a pale vapour, which escapes from the tube in bluish flames; and when the evaporation of the phosphorus is considerable, frequently ignites spontaneously. With sulphuret of carbon, long luminous clouds are formed, which rise several feet above the exit aperture, and may be set light to at a great distance. Nevertheless the phosphorus can be made to diffuse light in the vapour of pure æther at an elevated temperature, but the phosphorus must be then heated to boiling.

The luminosity of phosphorus in the air or in oxygen is totally different, as here a true combustion always occurs. The lustre of the phosphorus is also different. Gases which have been passed over phosphorus likewise exhibit a similar luminosity when they come in contact with the air; we now find ozone in them, and acid is detected by litmus. In dry oxygen the phosphorus does not continue to give light for a very long time, for this reason, that it soon becomes coated with a crust of oxide, which prevents the evaporation.

According to Schönbein, pure oxygen furnishes no ozone; this statement is confirmed when the experiment is made in the usual manner, but phosphorus gives light in a current of oxygen, and likewise forms ozone. It ceases to light, it is true, after a time, and with it the production of ozone, owing to the formation of a crust of oxide; but both recommence when the phosphorus is heated just sufficiently to break the crust without igniting it.

Phosphorus continues to give light in a current of oxygen for a short time at 10°. It is extinguished by the vapour of æther and other substances. A strong current overcomes this; in a current of air it is extinguished below a temperature of 27°.

When phosphorus continues to give light at a low temperature in the air, this does not result from oxidation, as no oxygen is absorbed

in this case; the vapour of phosphorus mixes with the air, and becomes luminous on its expansion *in vacuo*, or by the access of other gases, hydrogen or nitrogen.

The luminosity of other substances allied to phosphorus is not identical with the above; with these bodies the light always appears to stand in some relation with a slight oxidation.—*Journ. für Prakt. Chem.*, l. p. 1.

Observations on Phloridzine. *By* G. Roser.

In 1839, Stass published a long memoir on phloridzine. He advanced for it a formula which Liebig was induced to modify. The apparent affinity of phloridzine to salicine led him to select a formula which differed only by containing 2 equivs. more oxygen from the formula of salicine then admitted; and the formula proposed by him agreed better with the results of an analysis of a lead compound of phloridzine. Since that time the question has remained undecided, and it appeared therefore desirable to make a fresh examination, in order to ascertain which of the two formulæ was correct.

A large amount of crude phloridzine, which had been prepared in the laboratory of Giessen on a former occasion, was placed at my disposal. It was of a dark colour, from the admixture of an extractive substance, which could not be entirely removed by recrystallization and treatment with animal charcoal. The following method was therefore adopted to purify it:—The phloridzine was dissolved in hot water, and boiled for some time with the addition of a little gelatine, when the greater portion of the foreign substance adhered to the sides of the vessel in the form of a tenacious brown mass. The decanted liquid was then mixed with alum and neutralized with lime; the precipitate again contained much foreign substance, and the crystals which now separated were tolerably free from colour. It was however only possible to obtain them perfectly pure by adding to the solution a few drops of basic acetate of lead, which precipitates the foreign substances before the phloridzine. The crystals which separate from the solution, acidified with some acetic acid, were recrystallized until they left no ash on combustion. Elementary analysis furnished the same numbers as those obtained in former analyses, viz. 53·95 C, 6·17 H, and 39·88 per cent. O.

In order to determine the atomic weight, Stass prepared and analysed a lead compound of phloridzine. The results, however, as observed by Liebig, are somewhat unusual, 4 equivs. oxide of lead being assimilated for 3 equivs. water in the dry phloridzine. I have not obtained the same results as Stass, and have assured myself that several compounds of phloridzine with oxide of lead exist which are difficult to separate, and are therefore not suited for establishing the atomic weight. The silver compound decomposes so readily, that it also is not adapted for the determination of the atomic weight. I have therefore attempted to establish the formula of phloridzine by a different method. When phloridzine is heated with dilute mu-

riatic or sulphuric acid, it is decomposed into sugar and phloretine, which separates, no other body being formed. Supposing it possible to determine accurately the amount of sugar formed, we should thence readily be able to deduce the atomic weight of phloridzine.

To estimate the sugar, I first tried the method proposed by Krocker for the determination of the amount of starch in flour, &c. About 2 grms. of phloridzine were digested with dilute sulphuric acid, the phloretine separated after cooling by filtration, the solution of sugar mixed with the requisite amount of neutral tartrate of potash, and placed with some yeast in Fresenius's apparatus. All the precautions directed by Krocker were observed, but it was not possible to obtain accordant results.

I must observe, that I have never entirely succeeded in estimating starch according to Krocker's method, and of obtaining the accurate amount of carbonic acid corresponding to theory, nor did I succeed better in a test experiment with a weighed quantity of cane-sugar. The reason is undoubtedly, as stated by Fehling, owing to the conversion of the cane-sugar into grape-sugar by acids not taking place so readily and quickly as has hitherto been assumed. Moreover, the complete conversion of starch into sugar by sulphuric acid is frequently accompanied by difficulties, and the reaction with iodine, which Krocker employs to ascertain its complete metamorphosis, is by no means so accurate, and is moreover very deceptive.

A second method of estimating sugar is by means of a normal solution of copper, which has recently been much employed. The phloridzine was decomposed by sulphuric acid, the solution filtered from phloretine saturated with soda suitably diluted, and then added to 10 cub. centim. of the copper solution until these were entirely decomposed. I obtained in this manner accordant results, but not the amount of sugar which certainly should have been obtained admitting either of the formulæ for phloridzine. The error lay in the preparation of the test solution of sugar used to ascertain the strength of the copper liquid. It is absolutely necessary to employ pure grape-sugar for the purpose, and the plan of converting cane-sugar by an acid into grape-sugar should be rejected. It was moreover found that the phloridzine required long digestion with acid to decompose it entirely, for I always found more sugar the longer the digestion was continued, until finally, after four days' standing, a maximum was attained, and the quantity again decreased if the experiment was further continued.

0·6–1·0 grm. of dry phloridzine were treated with about 20 grms. of water, 50 drops of dilute sulphuric acid added, and then left for four days on the water-bath. After cooling, the phloretine was collected on a filter, and washed until the sulphuric acid was entirely removed. The solution was then saturated with soda, diluted so as to form a certain volume (150 or 200 cub. centim.), and now poured from a burette into the boiling copper solution (10 cub. centim.) until this was completely decolorized, and the whole of the copper thrown down as protoxide. This is easily ascertained by filtering a sample, and testing it with ferrocyanide of potassium and a few

drops of muriatic acid. This reaction is more sensitive than that with sulphuretted hydrogen. The plan proposed by Kersting, of using paper which has been immersed in ferrocyanide of potassium, is not applicable, as the liquid to be tested is strongly alkaline, and ferrocyanide of potassium will not detect copper in such solutions.

It will be understood that I examined the phloridzine and the phloretine separately, to ascertain whether they exerted any decomposing action upon the solution of copper; but this was not in the least the case. In this manner I obtained as the mean of eight experiments 41·76 per cent. of sugar, which agrees pretty closely with Liebig's formula, according to which phloridzine, $C^{42}H^{25}O^{20}$, furnishes on its decomposition 1 equiv. sugar, $C^{12}H^{12}O^{12}$, or 41·19 per cent. According to Stass, 1 equiv. dry phloridzine, $C^{32}H^{18}O^{15}$, furnishes $\frac{2}{3}$ equiv. sugar, $C^{8}H^{8}O^{8}$, which would correspond to 36·36 per cent.

Admitting that an equivalent of grape-sugar is formed on the decomposition of phloridzine, the 16·7 per cent. carbon contained in 41·76 per cent. of sugar correspond to 12 equivs. For the second product of the decomposition of phloridzine, the phloretine, there remain 58·3−16·7=41·6 C, which, if 17·6=12 equivs. (29·89), must correspond to 30 equivs. C. According to this, we have for phloretine the formula $C^{30}H^{15}O^{10}$, as it furnishes on analysis numbers the simplest expression for which would be $C^{6}H^{3}O^{2}$. I obtained the following numbers, using oxide of copper and chlorate of potash for the combustion:—

Carbon	65·35	65·03	65·41
Hydrogen	5·31	5·21	5·41
Oxygen	29·39	29·76	29·09

Dry phloridzine should therefore have the formula $C^{42}H^{25}O^{20}$, which agrees with the results of different chemists; in the crystallized state it contains 4 equivs. water $=C^{42}H^{29}O^{24}$. Phloretine is very sparingly soluble in cold water; it was therefore possible to check the above result by collecting and determining its amount. Phloridzine gave, as a mean of nine experiments, 60·46 per cent. of phloretine; theory requires 62·9 per cent.; but as it is not quite insoluble in water, the whole amount was not obtained. According to Stass's formula, there is formed from $C^{32}H^{18}O^{15}$—

Sugar ..... $C^{8}H^{8}O^{8}$
Phloretine..... $C^{24}H^{11}O^{8}$ = 66·09 per cent. phloretine.

I also attempted to determine the amount of sugar which is formed by the analogous decomposition of salicine. But the complete decomposition of salicine is so difficult and so slow, that I was not surprised at never obtaining coincident results. If I had succeeded in confirming in this manner the known composition of salicine, it would certainly have been the best proof that the atomic weight of phloridzine may be correctly found by this method.

As salicine is so difficult to decompose entirely by acids in its aqueous solution, I tried to accomplish it by passing hydrochloric

acid gas into an alcoholic solution. In this operation a splendid purple liquid formed, which on being mixed with water deposited a red powder, which possessed the composition and properties of the salicetine described by Piria.—Liebig's *Annalen*, lxxiv. p. 178.

On Stibæthyle. *By* C. Löwig *and* E. Schweitzer.

[Continued from page 377.]

Stibæthyle and Sulphur, $StäS^2$.—When stibæthyle is placed in contact with sulphur under water, combination immediately results with evolution of heat. If the mixture be warmed, and the aqueous solution then decanted from the excess of sulphur and evaporated, the sulphuret of stibæthyle is obtained in crystals. This compound is most quickly procured by boiling an ætherial solution of stibæthyle in a small flask with washed and well-dried flowers of sulphur. On pouring the still warm ætherial solution from the excess of the sulphur, the whole liquid congeals in a few minutes to a mass of dazzling white acicular crystals. The mother-liquor is allowed to drain off, and the crystalline mass exposed for some time to the air in order to oxidize the still-adherent stibæthyle; after which it is again dissolved in warm æther, and the perfectly pure compound obtained by repeated crystallization.

The sulphuret is the most beautiful of the compounds of stibæthyle which has hitherto been obtained. When dry, it forms a very bulky crystalline mass, with a silvery lustre, of a disagreeable, faint, mercaptan-like odour, and a bitter taste resembling slightly that of sulphuret of potassium; it is easily soluble in water and in alcohol, and also in hot æther, but very sparingly soluble in cold; it melts above 212° to a colourless liquid, which solidifies on cooling to a crystalline mass. The perfectly dry sulphuret of stibæthyle experiences no change in the air. When heated above its melting-point, it is decomposed with the formation of a liquid product which has the greatest resemblance to sulphuret of æthyle. When a piece of potassium is placed in melted sulphuret of stibæthyle, vapour of stibæthyle is immediately given off, and ignites in the air.

The aqueous solution of the sulphuret of stibæthyle precipitates all metallic salts as sulphurets, and this compound is therefore best adapted for the preparation of the salts of the oxide of stibæthyle. Dilute acids immediately disengage sulphuretted hydrogen. The entire behaviour of this compound is so analogous to that of the sulphuret of potassium, that the analogy between the latter and sulphuret of sodium cannot be called greater.

The combustion was made in the usual way with the oxide of copper, and the sulphur determined, as in the case of the metallic sulphurets, by oxidation with strong nitric acid. Fuming acid must not be employed, as this produces inflammation. An acid of 1·42 spec. grav. is best adapted for the purpose; at first, however, there is always a portion of sulphur eliminated. The analyses gave—

Carbon.....	29·06	29·12	12 =	72	29·03
Hydrogen	6·25	6·24	15	15	6·05
Antimony	51·60	51·62	1	129	52·01
Sulphur	13·09	13·02	2	32	12·91
	100·00	100·00		248	100·00

Stibæthyle and Selenium, $StäSe^2$.—Selenium behaves precisely like sulphur towards stibæthyle. If an ætherial solution of stibæthyle be boiled with precipitated selenium, the seleniuret crystallizes during the cooling precisely like the sulphuret of stibæthyle, with which in fact it agrees in its essential characters. However, the seleniuret very soon undergoes decomposition by exposure to the air, selenium being separated. The authors have not analysed this compound; from its analogy with the sulphuret, the composition is—

Carbon	12 =	72	24·32
Hydrogen	15	15	5·06
Antimony	1	129	43·59
Selenium	2	80	27·03

Stibæthyle and Iodine, $Stäl^3$.—Iodine and stibæthyle combine instantly under water with considerable evolution of heat. On adding iodine to an ætherial solution of stibæthyle, violent ebullition suddenly results, and the iodine disappears as quickly as if it had been brought into a solution of pure potash. The iodide is best prepared by adding iodine to an alcoholic solution of stibæthyle, kept in a refrigerating mixture, in small quantities until its colour disappears, when the perfectly colourless solution obtained is left to spontaneous evaporation. The iodide of stibæthyle crystallizes from the solution in perfectly colourless transparent needles, frequently half an inch long, which are first recrystallized from an alcoholic, and then from an ætherial solution, in order to obtain the compound perfectly pure; this is requisite, as there is almost always formed a small quantity of a yellow powder insoluble in æther, which is a compound of iodine with stibæthyle. It was stated in the first memoir, that frequently colourless crystals are formed in stibæthyle, which contain iodine; these crystals are iodide of stibæthyle.

The iodide of stibæthyle has a slight odour of stibæthyle and a strong bitter taste; it is very readily dissolved by alcohol and æther, and is also soluble in water without decomposition. From the hot saturated aqueous solution the greater part again separates in crystals; a determination of the iodine in the compound separated from the aqueous solution gave the same result as the analysis of the crystals obtained from alcohol or æther. Iodide of stibæthyle melts above 159° F. to a perfectly colourless transparent liquid, which again solidifies to a crystalline mass at that temperature. If it be heated to 212°, and kept for some time at this temperature, a small portion sublimes unaltered; but if the temperature be only moderately increased, it is decomposed with formation of dense white fumes; no elimination of iodine is perceptible. Potassium imme-

diately effects the reduction of the fused iodide of stibæthyle. Towards metallic salts it behaves exactly like a solution of iodide of potassium; it produces a red precipitate in a solution of corrosive sublimate, which again entirely dissolves in excess. Muriatic acid decomposes the iodide of stibæthyle immediately, with formation of chloride of stibæthyle; chlorine and bromine liberate the iodine; nitric acid does the same, with formation of nitrate of the oxide of stibæthyle. Concentrated sulphuric acid immediately disengages a dense vapour of hydriodic acid, and at the same time iodine is set free, with production of sulphurous acid.

The combustion is easily made with oxide of copper when the front part of the tube is filled with copper turnings. The determination of the iodine was effected by nitrate of silver; the compound fused in the water-bath was dissolved in alcohol, and the solution precipitated with nitrate of silver. The alcoholic solution of the nitrate of the oxide of stibæthyle was first removed by filtration in the dark, and the iodide of silver washed, at first with a little alcohol, and then with water. There were found—

Carbon	14·94	15·05	14·60	15·11	12=	72	15·32
Hydrogen ..	3·27	3·21	3·24	3·26	15	15	3·19
Antimony ..	27·72	27·56	27·46	..	1	129	27·45
Iodine	54·07	54·18	53·70	..	2	254	54·04

Bromide of Stibæthyle, $StäBr^2$.—When stibæthyle is added to bromine, each drop that comes into contact with the bromine takes fire. The pure bromide is easily obtained in the following manner:—A recently prepared spirituous solution of bromine is gradually added to a spirituous solution of stibæthyle so long as its colour disappears. To avoid too violent a reaction, the vessel containing the solution of stibæthyle must be cooled by ice. The solution is mixed with a large quantity of water, which throws down the bromide as a perfectly colourless, transparent heavy liquid. It is washed a few times with water, placed with chloride of calcium, and then decanted from it after a few days. The compound can also be purified by precipitating it by water repeatedly from the alcoholic solution.

The bromide of stibæthyle is a colourless highly refractive liquid of 1·953 spec. grav. at 63°, which solidifies at 14° to a snow-white crystalline mass; it has a disagreeable turpentine-like odour when warmed; causes a flow of tears and violent sneezing, like chloral; it is entirely insoluble in water, but dissolves readily in alcohol and æther; it is completely precipitated by water from the alcoholic solution. The bromide of stibæthyle is not volatile; nothing passes over even with the vapour of water. It burns with a white flame, giving off copious acid fumes; when subjected to distillation, there is obtained, among other products, a liquid which fumes strongly, and possesses an insupportable odour of chloral. Concentrated sulphuric acid decomposes the compound, with disengagement of hydrobromic acid vapours; chlorine instantly separates bromine. Towards salts of the metals the alcoholic solution behaves just like

bromide of potassium. The bromide of stibæthyle was analysed in the same way as the iodide compound. There was obtained—

Carbon	18·87	19·05	18·94	12=	72	19·15
Hydrogen	4·35	4·25	4·01	15	15	4·00
Antimony	34·36	34·07	..	1	129	34·30
Bromine.....	42·42	42·63	..	2	160	42·55

Chloride of Stibæthyle, $StäCl^2$.—When stibæthyle is let fall drop by drop through a narrow tube into a balloon filled with chlorine, at the moment of contact the drops take fire, and burn with a bright smoky flame. When stibæthyle is conveyed into dry muriatic gas over quicksilver, the quicksilver rises immediately, the volume diminishes one-half, the residual gas is hydrogen, while chloride of stibæthyle is formed. At those places where the stibæthyle is in contact with the gas, a constant evolution of gas is perceptible, the mercury rising in the same proportion. When fuming hydrochloric acid is poured over stibæthyle, chloride of stibæthyle is likewise formed, with disengagement of hydrogen; at first the stibæthyle acquires a dark colour at the surface, but finally the chloride of stibæthyle appears perfectly colourless. The compound is easily obtained in the pure state by mixing the concentrated solution of the pure nitrate of the oxide of stibæthyle with strong muriatic acid; the chloride of stibæthyle immediately subsides as a colourless liquid. The compound is purified in the same way as the bromide. All the compounds hitherto described furnish the chloride of stibæthyle by treatment with muriatic acid. The chloride of stibæthyle is a perfectly colourless, highly refractive liquid of 1·540 spec. grav. at 63° F.; it has a strong smell of turpentine, is insoluble in water, but readily soluble in alcohol and æther; it is still liquid at 10° F. When the chloride is boiled with water, a small quantity seems to volatilize unaltered with the aqueous vapours. In the distillation similar phænomena occur as with the bromide of stibæthyle. Concentrated sulphuric acid mixed with chloride of stibæthyle immediately disengages muriatic gas with considerable evolution of heat, whilst on the opposite hand muriatic acid precipitates from the solution of the sulphate of the oxide of stibæthyle chloride of stibæthyle; the reason of this is owing to its insolubility. In other respects the chloride of stibæthyle behaves like chloride of potassium and chloride of sodium. Analysis gave—

Carbon	25·11	25·04	25·11	12=	72	25·17
Hydrogen	5·55	5·48	5·41	15	15	5·25
Antimony	45·27	45·20	45·28	1	129	45·45
Chlorine.....	24·63	24·28	24·20	2	71	24·72

Cyanide of Stibæthyle.—When 2 atoms of cyanide of mercury are mixed with 1 atom of sulphuret of stibæthyle, both in the aqueous solution, the liquid filtered from the sulphuret of mercury has the odour and taste of prussic acid in a remarkable degree; towards salts of the metals it behaves like a solution of cyanide of potassium; nitrate of silver immediately precipitates cyanide of silver. When the solution is mixed with protopersulphate of iron, prussian blue is

immediately formed; and on adding muriatic acid to the filtered liquid, chloride of stibæthyle subsides. It is evident from these reactions that the solution contains cyanide of stibæthyle. If however it be kept for twenty-four hours, these reactions no longer obtain; they disappear more quickly on heating the liquid. Hence it follows that after some time some metamorphosis results, in consequence of which the cyanide of stibæthyle disappears. If the altered liquid be boiled with potash, a copious disengagement of ammonia is observed.

When iodide of stibæthyle is added to an alcoholic solution of cyanide of mercury, the iodide of mercury precipitated in the beginning redissolves when the iodide of stibæthyle is added in larger quantity. A salt separates from the solution, on spontaneous evaporation, in small, sulphur-coloured, shining, hard crystals, which are entirely soluble in water and alcohol. On mixing some dilute muriatic acid with the aqueous solution, iodide of mercury is immediately precipitated, whilst chloride of stibæthyle and prussic acid are formed at the same time. These crystals undoubtedly consist of iodide of mercury and cyanide of stibæthyle, corresponding to the compounds of the iodide of mercury with cyanide of potassium.

[To be continued.]

Further Researches on the Production of Succinic Acid by Fermentation. *By* M. Dessaignes.

When I briefly announced the conversion of crude malate of lime into succinate by spontaneous fermentation, it was my intention to add subsequently to this first observation any facts which analogy might reveal. I had already made considerable progress in the investigation when a paper on the same subject by M. Liebig appeared. I should then have discontinued my researches had I not discovered some facts which have not been observed by the learned chemist of Giessen.

I employ crude caseine as ferment, mix it intimately with the water containing in solution or suspension the substance under experiment, and leave the whole, at the ordinary temperature of summer, for three weeks or a month. My experiments have extended to the neutral and perfectly pure malate of lime, the acid malate of lime, the malate of potash, the aspartates of potash and of lime, the fumarate of lime, the maleate of the same base, and the aconitate of lime extracted from *Aconitum napellus*. All these salts are easily converted into succinate under the influence of the fermentation of the caseine. Asparagine begins, under the same influence, to change into aspartate of ammonia, which is then converted into succinate. If the fermentation is interrupted when it is still far from being complete, the liquid is found to contain a large quantity of aspartic and succinic acids at the same time.

The substance which exists in the seeds of the leguminous plants, and is converted in them into asparagine, is likewise susceptible of being changed into succinic acid. When some pea-flour is mixed

with water and left to fermentation, after the addition of some chalk a considerable quantity of succinate of lime will be found in the filtered liquid. I fermented separately the legumine, the liquid from which it had been precipitated, and also the nitrogenous substance which precipitates tannin, pointed out by M. Braconnot. I hoped thus to discover the substance which produces the succinic acid. Succinic acid was formed in all these fermentations, in unequal quantity, it is true; however, this part of my researches is not yet complete. I have also produced the same acid by the fermentation of the emulsion of sweet almonds, separated from its oil and mixed with chalk. It appears therefore that the succinic fermentation occurs as frequently in nature as the acetic, metacetic, butyric and valerianic fermentations.

I will now add a word on the isomeric acids of the formula $C^4 H^2 O^4$. As above seen, the fumaric, maleic and aconitic acids are equally converted into succinic acid. This similitude of transformation is remarkable; for, on the one hand, the citrates of lime and soda, when fermented with caseine, do not yield succinic acid; and, on the other, the two acids derived from malic acid are very precisely distinguished from aconitic acid by another metamorphosis. I have found that the bifumarate and the bimaleate of ammonia furnish on dry distillation a substance which is very similar in most of its reactions, but not identical with that which the bimalate of ammonia produces under the same circumstances. This substance, by the prolonged action of hydrochloric acid, is converted into aspartic acid, which is absolutely the same as that obtained with malic acid. Now the biaconitate and the biequisetate of ammonia do not produce aspartic acid when submitted to the same treatment. The neutral maleate of ammonia does not precipitate the perchloride of iron, whilst the neutral aconitate and equisetate of ammonia do. In the comparative examination of these three acids which I had entered upon, I was soon convinced of the perfect identity of the aconitic and the equisetic acids, and of the non-identity of the latter and maleic acid. However, the recent notice of M. Baup on this subject renders the publication of the details unnecessary.

I shall conclude by describing a method of obtaining with asparagine an aspartic acid crystallizing in the same form as the aspartic acid obtained from the bimalate of ammonia. Aspartate of ammonia derived from asparagine is heated to 392° until no further ammoniacal odour is perceived; a sparingly soluble brown substance is left, which, on being treated with hydrochloric acid, furnishes aspartic acid in short hard prisms, like those of the acid derived from malic, maleic and fumaric acids.—*Comptes Rendus*, Sept. 16, 1850.

On the Acid of Equisetum fluviatile *and some Aconitates.*
By M. Baup.

Some doubt existed as to the identity of the aconitic and equisetic acids, and the pyrogenous citridic and maleic acids. M. Baup has

endeavoured to throw some light on this question, and with this object in view has extracted the acid from the marestail (*Equisetum fluviatile*) and from monkshood (*Aconitum napellus*), and has compared them with the pyrogenous citric acid, called citridic, and with maleic acid. From the comparative examination which he has made of their properties and of several of their compounds, he concludes that the aconitic, equisetic and citridic are decidedly one and the same acid, which should be exclusively called aconitic acid, from whatever source derived. Maleic acid, although isomeric with it is not however identical, and should retain its name.

In examining several of the aconitates, M. Baup met with a fact which deserves the attention of chemists, as being the first example of a compound of 3 atoms of an organic acid to 1 of base. The trisaconitate of potash and that of ammonia have but a very small number of representatives in inorganic chemistry, for instance the trisiodate of potash of Serullas.

In his examination of the *Equisetum*, M. Baup discovered a peculiar yellow crystalline substance, which imparted to alumed cotton a yellow colour not inferior to that of woad. He has given it the name of *flavoquisetine*.—*Comptes Rendus*, Sept. 9, 1850.

On the Atomic Weight of Tungsten. By Dr. R. Schneider.

Berzelius first determined the number 1183·3 to be the equivalent of tungsten. The author has recently made some fresh determinations of the atomic weight, employing in general the same method which Berzelius followed for the purpose, determining the loss in weight which the tungstic acid experiences on being heated to redness in hydrogen, and the increase in the reduced metal after its oxidation at a red heat. The author adopted the following method for preparing and purifying the tungstic acid intended for these experiments. Native wolfram from Zinnwald was converted into as fine a powder as possible, and boiled for a considerable length of time in a flask with muriatic acid to which some nitric acid had been added. After the concentrated solutions of oxides of iron and manganese had been decanted several times, with fresh renewal of the acids, and the residue had acquired a tolerably pure lemon colour, it was collected on a filter, and the tungstic acid washed with warm water. The impure tungstic acid was now dissolved in ammonia; the ammoniacal solution, evaporated at a gentle heat to crystallization, furnished a salt which was recognised as the bitungstate of ammonia by its crystalline form. It was found impossible to obtain this salt, perfectly free from the oxides of iron and manganese, by repeated crystallization, although the operation was repeated five or six times, and the last crystallizations were obtained of a pure white colour. An equally unsuccessful attempt was made to remove these oxides by treating the tungstic acid precipitated from the solution of the tungstate of ammonia by muriatic acid with sulphuret of ammonium. It was found that a concentrated solution of the sulphuret of ammonium and tungsten, especially on being heated, takes up a small amount of sulphuret of

iron and sulphuret of manganese. The author finally succeeded in the following manner:—The tungstic acid separated from the solution of the sulphuret of ammonium and tungsten was boiled for a long time with nitromuriatic acid, the contents of the flask then diluted with water, filtered, and the tungstic acid washed with acidified water as long as it removed any oxide of iron; upon this it was taken from the filter and warmed with dilute solution of ammonia, which left a slight bluish-gray residue, which was separated by filtration. The colourless solution was mixed with an excess of muriatic acid, and the precipitate of tungstic acid treated in the way above described with aqua regia and ammonia. After this operation had been repeated three times more, a tungstic acid was obtained, in which no longer a trace of oxide of iron could be detected. A sample, heated with a solution of chemically pure potash, gave a perfectly clear colourless solution, from which after some days' standing not a trace of a brown flocculent precipitate was deposited; nor could a trace of iron be discovered in the last wash-water by the most sensitive reagent. The acid so obtained was dried, rubbed to a fine powder, and exposed to an intense red heat in a porcelain crucible. Whilst hot, it exhibited an intense lemon colour, which on cooling became slightly paler, and at the same time acquired a faint greenish tint. After this treatment, the acid from the wolfram of Zinnwald was considered pure, as the presence of other metals which the mineral might contain is excluded by the method pursued. This applies especially to tin, molybdenum, tantalum and its allies.

The tungstic acid so purified was now reduced in quantities of 2 to 6 grms. in hydrogen; and, on the other hand, the metal so obtained again oxidized. The metal, after it had been heated once more in a current of hydrogen and allowed to cool, was heated in a porcelain crucible over an Argand lamp, at first gently, and the heat gradually raised to a faint red. The metallic tungsten, prepared by reduction in a current of hydrogen, can be completely oxidized into acid by calcination in the air. In this operation it burns like tinder, and increases considerably in bulk, without giving off the least dust, when the temperature is carefully raised. However, in order that the oxidation may be complete, it is necessary to apply the heat for a considerable time, as the tungstic acid first formed incloses small traces of unaltered metal, and protects them from the oxidizing influence of the air. The oxidation can be hastened by the addition of a few drops of nitric acid; it is nevertheless requisite to ascertain, by repeated heating and weighing, whether the whole of the metal has been converted into acid. The following are the results obtained in this manner:—

I. *By Reduction.*

1.	In 100 parts tungstic acid	79·336	tungsten.
2.	... ...	79·254	...
3.	... ...	79·312	...
4.	... ...	79·326	...
5.	... ...	79·350	...
Mean		79·316	

II. *By Oxidation.*

1. In 100 parts tungstic acid	79·329	tungsten.
2.	79·324	...
3.	79·328	...
Mean.....	79·327	

From the reduction experiments we obtain—

As atomic weight the number	1150·39
From the oxidation experiments the number	1151·17
The mean from the two is.....	1150·78

According to this, the per-centage composition of tungstic acid and of the oxide of tungsten is—

Tungsten	79·321	85·193
Oxygen	20·679	14·807

Previous to making the above determinations, the author had completed an examination on the constitution of the mineral wolfram. Berzelius first regarded this mineral as a neutral compound of tungstic acid with the protoxides of manganese and iron. Count Schaffgotsch concluded, from his numerous analyses of this mineral, that it did not contain tungstic acid, but the oxide of tungsten. This result however may be owing to errors in the analyses, this chemist having considered the yellow powder which remained after treating the mineral with muriatic acid to be pure tungstic acid. No regard was had to the undecomposed portion of the mineral, nor to the quartzose ingredients, which almost constantly accompany wolfram, and are so minutely distributed through the mass generally in the form of delicate laminæ, that it is not possible, even with the greatest care, to separate them completely. He moreover appears to have considered the substance left on calcining the residue of the liquid from which the iron and manganese had been precipitated as sulphurets, to be pure tungstic acid; this residue however consisted, as evident from the analyses of M. Ebelmen and the author, in part of earthy sulphates. He was led to the above conclusion from the circumstance, that in all his analyses he obtained a total excess of several per cents. when the amount of tungsten in the mineral was calculated as tungstic acid, which excess was not found when oxide was assumed to be present in the mineral. Moreover, its amount of oxygen was found to stand in a very simple relation to that contained in the bases; whilst, on the assumption of tungstic acid, this relation could only be remotely expressed by entire numbers.

Ebelmen subsequently showed, by the analysis of two wolframs from Zinnwald and Limoges, that the wolfram may nevertheless be calculated as tungstic acid without an excess in the analysis resulting. He obtained—

I. *Tungsten from Limoges.*

Tungstic acid	76·20	..	15·759
Protoxide of iron	19·19	4·264	
Protoxide of manganese.....	4·48	1·001	5·575
Magnesia.....	0·80	0·310	
	100·67		

II. *Tungsten from Zinnwald.*

Tungstic acid	75·99	..	15·715
Protoxide of iron	9·62	2·138	
Protoxide of manganese	13·96	3·139	5·412
Lime	0·48	0·135	
	100·05		

The first of these two analyses leads to the formula $4(FeO, WO^3) + MnO, MgO, WO^3$.

The author has examined some wolframs from the Hartz, following very nearly the same method as that adopted by Ebelmen. He arrived, with Berzelius and Ebelmen, at the result, that wolfram must be regarded as a neutral tungstate of the protoxides of iron and manganese of the formula RO, WO^3.

The author used for analysis some of the purest fragments of wolfram, which were reduced to a fine powder, and boiled with muriatic acid to which some nitric acid was added until the separated tungstic acid appeared of a pure lemon colour. The solution of chloride of iron and manganese, after being strongly diluted with water, was filtered from the tungstic acid, and the latter washed with acidified water until the liquid which passed off no longer showed the presence of iron. It was found also in the present case impossible to remove the last traces of the oxides of iron and manganese from the separated tungstic acid by means of acids; but unless this is done, on treating the tungstic acid with dilute caustic ammonia, they pass into solution with the tungstic acid, and are contained in it after evaporation and calcination. The acid was therefore after each weighing boiled with dilute caustic potash, when a few milligrammes of oxide of iron and manganese were always separated. The washed tungstic acid was removed from the filter by careful spirting; but the latter, in order not to lose any adherent traces of tungstic acid, was washed for some time with water containing a little ammonia, and the tungstic acid then digested with dilute ammonia. The ammoniacal solution was filtered, the insoluble residue well washed, weighed, and the weight deducted from that of the quantity of mineral used for analysis. This residue, which contains the whole of the silica mechanically enclosed in the mineral, must not be looked upon as a mixture of silica and undecomposed wolfram; it contains a larger amount of tungstic acid in proportion to the bases than the mineral itself. It seems consequently as if the decomposition of wolfram by acids was not quite uniform, the amount of the dissolved bases being somewhat greater than it should be compared with the amount of eliminated tungstic acid.

The ammoniacal solution of the tungstic acid was evaporated to dryness in the water-bath, the residue converted by calcination into tungstic acid, and then weighed. The minute quantities of the oxides of iron and manganese separated in treating the tungstic acid with caustic potash were dissolved in muriatic acid, and added to the principal solution of these metallic oxides. After the greater portion of the excess of acid had been expelled by evaporation, the iron and manganese were precipitated with sulphuret of ammonium;

the sulphurets, after being washed, decomposed by muriatic acid, and the oxides separated from each other by succinate or benzoate of ammonia. The liquid filtered from the sulphurets was evaporated to dryness, the residue heated to redness in a platinum dish, and then treated with dilute muriatic acid. The insoluble residue consisted of tungstic acid, the quantity of which was determined, and added to that previously obtained. The acid solution filtered from the small quantity of tungstic acid was neutralized with ammonia, the lime precipitated by oxalate of ammonia, and then the magnesia by phosphate of soda. The following are the results of the analyses :—

Wolfram from Zinnwald.—It has the formula $2(FeO, WO^3)+3(MnO, WO^3)$ according to the following analysis :—

			Oxygen.
Tungstic acid	76·01	..	15·719
Protoxide of iron	9·81	2·108	
Protoxide of manganese	13·90	3·126	5·646
Lime	1·19	0·340	
	100·91		

Wolfram from Glasebach by Strassberg, Hartz.—The analysis leads to the formula $4(FeO, WO^3)+MnO, WO^3$:—

			Oxygen.
Tungstic acid	76·04	..	15·726
Protoxide of iron	19·61	4·357	
Protoxide of manganese	4·98	1·119	5·556
Lime	0·28	0·080	
Magnesia.....	a trace		
	100·92		

Wolfram from Pfaffenberg near Neudorf, Hartz.—Formula, $4(FeO, WO^3)+MnO, WO^3$:—

			Oxygen.
Tungstic acid	76·21	..	15·761
Protoxide of iron	18·54	4·120	
Protoxide of manganese	5·23	1·176	5·554
Lime	0·40	0·114	
Magnesia.....	0·36	0·144	
	100·74		

Wolfram from Meiseberg near Neudorf, Hartz.—The results of the analyses of this mineral differ slightly from the preceding, and may be best expressed by the formula $5(FeO, WO^3)+MnO, WO^3$:—

	I.	II.	III.	Mean.		Oxygen.
Tungstic acid.....	76·18	76·30	76·27	76·25	..	15·769
Protoxide of iron	20·31	20·12	20·38	20·27	4·501	
Protoxide of manganese	..	4·12	3·80	3·96	0·890	5·534
Lime	0·27	0·38	0·20	0·28	0·080	
Magnesia	0·08	0·16	0·07	0·15	0·060	
				100·91		

With respect to this difference in the formulæ, the author leaves it undecided whether it really be so in nature, or may be subsequently removed by a better method of analysis. But this at least is certain, that wolfram does not contain oxide, but tungstic acid; as in a direct experiment, by fusing the mineral with carbonate of soda and excluding the air, the author obtained tungstate of soda.

Lastly, with respect to Margueritte's view regarding the constitution of wolfram, that it consists of R^2O^3, W^2O^5, in which R^2O^3 denote the bases peroxide of iron and manganese, the author has proved the incorrectness of this view by decomposing the mineral with muriatic acid in a suitable apparatus in which the air had been entirely expelled by carbonic acid, and showing the solution to contain only protoxide and no peroxide of iron. There remains no doubt as to the manganese being contained in the state of protoxide in wolfram, which must consequently be expressed by the formula RO, WO^3.—*Journ. für Prakt. Chem.*, vol. xlix. p. 321.

On the Precipitation of Morphine by Charcoal. *By* M. Diesel.

The author has endeavoured to precipitate morphine from a muriatic extract of opium by means of animal charcoal. The result was however unsuccessful; the charcoal takes up the morphine, but can only be in part reobtained by exhaustion with boiling alcohol. —*Archiv der Pharm.*, lxii. p. 162.

Ready Method of preparing Helenine. *By* W. Delffs.

When the fresh root of *Inula Helenium*, cut in slices, is exhausted with boiling alcohol of 0·833 spec. grav., and the hot filtered solution is mixed with from 3 to 4 times its bulk of cold water, a slight turbidness results; and after twenty-four hours, dazzling white needles, several inches in length, of pure helenine, will be found in the liquid. The mother-liquor retains so little helenine, that it is scarcely worth while evaporating it. The experiment also succeeded with the dried root which had been kept for half a year, but the produce appeared to be smaller. The root employed for these experiments had been collected towards the end of October.—Poggendorff's *Annalen*, 1850, No. vii.

ANALYTICAL CHEMISTRY.

On the Employment of Fluosilicic Acid in Quantitative Analysis. *By* Prof. H. Rose.

After Berzelius had prepared the fluosilicate of potash, and had drawn attention to its remarkable properties, chemists turned the sparing solubility of this salt to account, in order to separate several

acids from potash by fluosilicic acid, and to prepare them in a pure state. In this manner the chloric, perchloric, chromic, and other acids have been separated from potash. But the fluosilicic acid has never been employed in quantitative analysis for the complete separation of potash, because the fluosilicate of potash is only very sparingly soluble, and not entirely insoluble in water. Berzelius himself observes, that it will never be possible to employ it for the quantitative determination of potash. But the fluosilicate of potash is perfectly insoluble in a liquid which has been mixed with some alcohol; when therefore the solution of a salt of potash is mixed with fluosilicic acid, and an equal volume of strong alcohol added, the whole of the potash is precipitated as fluosilicate of potash, which is washed with strong alcohol diluted with an equal volume of water.

M. Weber obtained by this method from 1·548 grm. fused chloride of potassium, 2·307 fluosilicate of potash, which was dried at 212° upon a weighed filter. The quantity of chloride of potassium employed corresponds to 2·293 fluosilicate of potash. The fluosilicic acid may therefore be employed successfully for the quantitative determination of potash.

Soda may likewise be accurately estimated according to the same method. M. Weber obtained, on mixing a solution of 2·038 grs. of chloride of sodium in water with fluosilicic acid, a precipitate, which however was much increased by the addition of strong alcohol. It was washed with dilute alcohol, and dried at 212° upon a weighed filter. It amounted to 3·2977 grms. The fluosilicate of soda contains 0·809 sodium, whilst the chloride of sodium used contains 0·808.

Berzelius turned to account the insolubility of the fluosilicate of baryta, for separating qualitatively and quantitatively baryta from strontia by fluosilicic acid. This method is certainly the best we are acquainted with; but when baryta is precipitated by fluosilicic acid from an aqueous solution, there is a loss owing to the fluosilicate of baryta not being entirely insoluble in the water; if it be precipitated from a spirituous solution, the result is perfectly accurate. From 1·820 grm. chloride of barium, dissolved in water, and precipitated with pure fluosilicic acid with the addition of a little dilute alcohol, 2·458 fluosilicate of baryta were obtained, which were dried on a weighed filter at 212°. They correspond to 1·344 grm. baryta, and the quantity of chloride of barium used to 1·340.

Whilst in the precipitation of the fluosilicate of potash and soda the aqueous liquid must be diluted with an equal volume of strong alcohol in order to precipitate these salts entirely, a very small quantity of alcohol is needed for the precipitation of the fluosilicate of baryta.

In the application of fluosilicic acid to quantitative investigations, one circumstance should be mentioned which deserves the greatest attention. In all the manuals of chemistry it is stated, that dilute fluosilicic acid does not in the least attack glass in the cold,

and that this only happens on evaporation in glass vessels; this however is not correct. When very dilute fluosilicic acid has been kept for a long time in glass vessels, it is not pure; and although the inner surface of the glass does not appear to be attacked, the acid has deprived the glass of some alkali, lime and oxide of iron, if the glass contained any of the latter. In such circumstances we often find a sediment of alkaline fluosilicates in the acid. Now if such an acid be used to precipitate the alkalies and baryta, the alcohol likewise throws down the alkaline fluosilicates held in solution, and an excess is obtained. An acid which has been kept for any length of time in glass vessels is still good for many qualitative examinations, especially for the easy discrimination of strontia from baryta, but not for quantitative determinations, for which indeed fresh fluosilicic acid must be prepared for each analysis, provided it can be done, unless kept in platinum or silver vessels.

On precipitating 1·157 grm. chloride of barium in an aqueous solution by fluosilicic acid, which had been kept, probably for some years, in glass vessels, 1·636 grm. fluosilicate of baryta was obtained on the application of alcohol. This corresponds to 0·894 baryta, whilst the chloride of barium used contains only 0·851 baryta. The fluosilicate of baryta however contained the alkaline fluosilicates which had been dissolved by the fluosilicic acid, and were precipitated by the alcohol.

Fluosilicic gas likewise attacks glass, though but very faintly; consequently when silicates containing fluorine, or rocks in which phosphates containing fluorine, for instance apatite, occur along with silicates, are decomposed in the pulverized state with concentrated sulphuric acid, notwithstanding the large excess of silica in the decomposed mass, a slight etching may be produced upon glass by the evolved vapour. But the etching is certainly so faint, that it is frequently not observed by inexperienced persons, and is only rendered visible by breathing upon the glass. The fluoride of silicon is decomposed, even by a very minute trace of moisture, at a gentle heat; therefore fluoride of silicon, and subsequently some hydrofluoric acid (which latter causes the etching), escapes from the decomposed mass.—Poggendorff's *Annalen*, No. vii. 1850.

On the Detection of Strychnine. *By* A. W. Brieger.

The reaction of substances containing much oxygen upon strychnine is very distinct with pure chromic acid, far more so than with the bichromate of potash, first recommended for the purpose by Otto. By means of this reaction it is possible to detect strychnine when mixed with santonine, brucine, &c. But several substances prevent the appearance of the violet colour more or less, for instance pure or acetate of morphine; quinine renders the colour pale rosered; sugar conceals the reaction.—*Jahrb. für Prakt. Pharm.*, xx p. 87.

THE CHEMICAL GAZETTE.

No. CXCIII.—November 1, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the artificial Formation of Lactic Acid, and a new Substance homologous with Glycocoll. *By* Dr. A. STRECKER.

THE investigations of Engelhardt and of Städeler on the metamorphoses of lactic acid, have shown that aldehyde (or its derivative compounds) is one of the most common products of this acid. Liebig had already observed, that lactic acid furnishes, on oxidation with manganese and sulphuric acid, or with peroxide of lead, a large amount of aldehyde, with the simultaneous disengagement of carbonic acid. It seemed therefore not improbable that lactic acid was a conjugate compound of aldehyde and formic acid, just as formobenzoilic acid may be viewed as a conjugate compound of formic acid with the aldehyde of benzoic acid :—

$$C^2 H^2 O^4 + C^4 H^4 O^2 = C^6 H^6 O^6.$$

Formic acid. Aldehyde. Lactic acid.

$$C^2 H^2 O^4 + C^{14} H^6 O^2 = C^{16} H^8 O^6.$$

Formic acid. Oil bitter alm. Formobenz. acid.

As is well known, formobenzoilic acid is resolved, on treatment with oxidizing agents, in like manner into carbonic acid, water and oil of bitter almonds.

The formobenzoilic acid is formed by the union of oil of bitter almonds with formic acid *in statu nascenti*, the latter acid being generated by the action of muriatic acid upon prussic acid in the presence of oil of bitter almonds. It appeared therefore possible that lactic acid might be obtained by the same reaction, on substituting aldehyde for the oil of bitter almonds. This supposition is confirmed by experiment. I have prepared lactic acid artificially in this way, not in so simple a manner as I expected, but by a more circuitous method; which however led me to the discovery of a substance which is in several respects highly interesting.

Behaviour of Prussic Acid towards Aldehyde-Ammonia.—When aldehyde-ammonia is mixed with an aqueous solution of prussic acid, and the mixture left for some time in closed vessels, the decomposition which prussic acid undergoes when alone proceeds far more rapidly, so that generally, in the course of twelve hours, the prussic acid is destroyed, with separation of a brown powder (paracyanogen). If, on the contrary, the aqueous solution of aldehyde-ammonia and prussic acid is evaporated immediately on the water-bath, a brown thick syrup remains, which in the course of some hours congeals to a mass of slender needles, which are freed from colouring matter by

pressure between paper, and are obtained from solution in boiling æther on cooling as colourless, shining, slender needles. This substance is soluble in water, alcohol and æther; its aqueous solution gives no precipitate with salts of silver. By treatment with alkalies, it is resolved into various products, among which prussic acid, aldehyde and ammonia are readily detected. This body possesses basic properties, or at all events passes into a base on treatment with acids, and furnishes with chloride of platinum a readily soluble double salt. I have not yet examined it more accurately, but hope soon to communicate further information on the subject.

A totally distinct compound is produced from mixtures of aldehyde-ammonia and prussic acid in the presence of acids, viz. *alanine.* When an aqueous solution of 2 parts by weight of aldehyde-ammonia and 1 part anhydrous prussic acid is mixed with an excess of dilute muriatic acid, not a trace of aldehyde passes over into the receiver on applying heat to the retort. The distillate contains, besides muriatic, a small quantity of prussic acid, and, if the muriatic acid was very concentrated, some formic acid. On evaporating the liquid, which has been reduced to half its volume in the retort, on the water-bath, a large quantity of chloride of ammonium crystallizes out, and there remains a very acid thick mother-ley, which contains the muriatic compound of a new substance, which I will call *alanine.*

To separate the muriate of alanine from the large amount of chloride of ammonium with which it is mixed, the simplest plan is to add a little water to the mass, which has been freed as much as possible from excess of muriatic acid by long heating on the water-bath, and to filter from the undissolved chloride of ammonium, which latter is rinsed with a little cold water. The filtered liquid is freed from muriatic acid and chloride of ammonium by boiling with hydrated oxide of lead, which is suspended in water, and added to the boiling liquid from time to time until no further smell of ammonia is perceptible. The liquid now contains much oxide of lead in solution; it is filtered boiling-hot from the precipitated basic chloride of lead, and the lead in solution entirely precipitated by a current of sulphuretted hydrogen. The liquid filtered from the sulphuret of lead furnishes, on concentration and cooling, crystals of alanine. Some alanine is precipitated from the mother-liquor upon the addition of a little alcohol. The crystals are rinsed with a little alcohol, and so obtained perfectly free from muriatic acid. The last mother-liquors contain a little muriate of alanine, and sometimes some chloride of ammonium. Much of the hydrated oxide of lead may be spared if the mixture of muriate of alanine and chloride of ammonium is mixed with alcohol and some æther, in which the chloride of ammonium is very sparingly soluble, whilst the muriate of alanine is readily dissolved. After driving off the alcohol and æther, the solution is freed, by means of hydrated oxide of lead, from muriatic acid and a small quantity of ammonia.

From a hot saturated solution alanine crystallizes on cooling in colourless fasciculate prisms, which are generally acicular, but are

sometimes obtained of considerable size, and then appear to be oblique rhombic prisms. The surfaces of the crystals prepared by me were too rough to allow of their being measured. On evaporating the aqueous solution of alanine, a film forms on the surface, beneath which feathery crystals form. The larger crystals have a nacreous lustre, are hard, and grate between the teeth; they dissolve in 4·6 parts of water at 63° F.; more readily in hot, but only very sparingly in cold alcohol (in about 500 parts of alcohol of 0·863), and not at all in æther. The aqueous solution has a very sweet taste, no action upon vegetable colours, and does not furnish a precipitate with any of the usual reagents. When alanine is heated above 392°, it sublimes, and then falls in fine snowy crystals not far from the heated spot. When heated quickly, it melts, and undergoes partial decomposition; when heated quickly upon platinum foil, it burns with a violet flame. It furnished on analysis—

Carbon	40·60	40·09	6 =	36	40·45
Hydrogen	7·82	7·81	7	7	7·86
Nitrogen	..	15·52	1	14	15·73
Oxygen	..	..	4	32	35·96

leading to the formula $C^6 H^7 NO^4$.

Alanine is formed by the union of equal equivalents of aldehyde and hydrocyanic acid, and the assimilation of 2 equivs. water, according to the following equation:—

$$C^4 H^4 O^2 + C^2 NH + 2HO = C^6 H^7 NO^4.$$

The ammonia of the aldehyde-ammonia unites with the muriatic acid. I have not been able to obtain any alanine by mixing aldehyde with prussic acid; the presence of muriatic acid appears requisite for the production of the compound.

The chemical formula of alanine agrees perfectly with the formula of three other bodies, *urethane*, *lactamide* and *sarcosine*. The two former are already distinguished from alanine by their melting below 212°, and moreover by numerous other physical and chemical characters; sarcosine, on the other hand, exhibits in many respects a close agreement with alanine. Its deportment towards various solvents and on being heated, its taste and power of combining with acids, might with superficial experiments lead to their being confounded; but, on careful examination, differences are readily perceptible. Sarcosine, for instance, is more easily soluble in water, and sublimes at 212°; its taste is far less sweet and more acrid. The distinctness of alanine from sarcosine will be more clearly pointed out in the following pages; but the property which alanine has of forming compounds with bases is that which most readily distinguishes it from sarcosine.

Compounds of Alanine with Acids.—Alanine dissolves more readily in dilute acids than in water, without however destroying their reaction upon vegetable colours, and upon the addition of alcohol no alanine is separated. If a solution of alanine in a very volatile acid be evaporated, a very acid mass remains, which is a compound of alanine with the acid employed. The compounds of

alanine with acids are all more easily soluble in alcohol than alanine itself; the majority likewise dissolve in a mixture of alcohol and æther.

Nitrate of Alanine.—On slowly evaporating a solution of alanine in dilute nitric acid, this salt remains in the form of colourless long needles. They deliquesce in moist air, and dissolve very readily in water, and somewhat less in alcohol. The crystals, dried over sulphuric acid, lose at 212° nothing in weight; but they gradually experience a change, which is rendered evident by their assuming a yellow colour.

The nitrate of alanine, dried at the ordinary temperature, possesses the formula $C^6 H^7 NO^4 + NO^6 H$, as evident from the following analysis. It furnished—

Carbon	23·90	6 =	36	23·68
Hydrogen	5·47	8	8	5·26
Nitrogen	..	2	28	18·42
Oxygen	..	10	80	52·64

Muriate of Alanine.—Alanine unites at least in two proportions with muriatic acid. When dry muriatic gas is passed over dry alanine, the acid is absorbed with considerable evolution of heat, and a compound is formed containing 2 equivs. alanine to 1 equiv. muriatic acid, which is very soluble in water, and but sparingly soluble in alcohol. The same compound is obtained by dissolving alanine in the theoretical quantity of muriatic acid, on evaporation, or by the addition of alcohol to the concentrated solution, in colourless acicular crystals.

1·964 grm. alanine absorbed, on treatment with dry muriatic acid, after removal of the excess of acid with dry air, 0·398 grm. of muriatic acid, or 20·3 per cent. The compound consequently possesses the formula $2(C^6 H^7 NO^4) + ClH$, according to which the increase should amount to 20·5 per cent.

A sample, crystallized on evaporation of a solution of alanine in an insufficient quantity of muriatic acid, gave on analysis 21·3 per cent. muriatic acid. It contains therefore the above compound, but contaminated by another containing more acid.

The compound remaining on evaporating a solution of alanine in an excess of muriatic acid to dryness is very difficult to obtain pure; it is exceedingly deliquescent, and dissolves even in alcohol with the greatest ease. A sample, dried at 212°, contained 30·2 per cent. of muriatic acid; the formula $C^6 H^7 NO^4 + ClH$ requires 29·1 per cent.

Neither the aqueous nor the alcoholic solution of the muriate of alanine furnishes a precipitate with chloride of platinum; but if the solution which has been mixed with chloride of platinum is evaporated, and the nearly dry mass treated with a mixture of alcohol and a little æther, and this solution allowed to evaporate spontaneously, slender yellow needles separate, which are soluble in water, alcohol, and even in a mixture of æther and alcohol. At 212° the crystals acquire a dark colour, and constantly decrease in weight.

After being kept for some time at 212°, they dissolve in water, leaving a residue of ammonio-chloride of platinum.

The crystals, freed by rinsing with æther and a little alcohol from chloride of platinum, and dried at the ordinary temperature, left on combustion 35·4 per cent. platinum. The formula $2(C^6 H^7 NO^4) + ClH + 2PtCl^2$ requires 35·6 platinum.

Alanine is readily distinguished from sarcosine by this platinum compound. The platino-chloride of sarcosine is insoluble in a mixture of alcohol and æther, and crystallizes in large octahedral crystals.

The *sulphate of alanine* is very readily soluble in water, and is left on evaporation as a syrupy mass, which solidifies into crystals only after long standing. It can be freed from excess of sulphuric acid by rinsing with a little alcohol. No sulphate of alanine is precipitated, even from the most concentrated aqueous solution, by the addition of absolute alcohol. A mixture of alcohol and æther separates the sulphate in the form of a thick syrup.

The extreme solubility of the compounds of alanine with acids, and the small quantity of material at my disposal, prevented a more accurate examination. From what has been stated above, it follows that the compounds of alanine with the oxyacids consist, like the salts of the organic bases, of alanine + the hydrate of the acid. From the muriate forming a compound with the chloride of platinum, it appears that alanine should be referred to the alkaloids, although it does not neutralize acids.

Compounds of Alanine with Metallic Oxides.

Alanine and Oxide of Copper.—An aqueous solution of alanine, on being boiled with oxide of copper, acquires a dark blue colour; and on evaporation, dark blue crystals separate, which are in part acicular, and appear under the microscope in the form of long six-sided tables. Part however formed thick rhombic prisms. This compound with alanine and oxide of copper is pretty soluble in water with an intense colour; the deep blue-coloured solution is rendered nearly colourless on the addition of nitric acid. The crystals are nearly insoluble in alcohol; they are not altered when heated to 212°, but at a higher temperature change their form, become light blue, and now furnish a bluish light powder. The formula of the crystallized alanine and oxide of copper is $C^6 H^7 NO^4 + CuO$.

At 248° the compound loses 1 atom of water, so that the dry salt is represented by the formula $C^6 H^6 NO^3, CuO$, as evident from the following analysis:—

Carbon.....	29·97	6 =	36	30·07
Hydrogen.....	5·17	6	6	5·01
Nitrogen	..	1	14	11·70
Oxygen.....	..	3	24	20·06
Oxide of copper	33·25	1	39·7	33·26

Alanine and Oxide of Silver.—When alanine is boiled with oxide of silver and water, a colourless solution is obtained, from which on

cooling yellowish needles, in hemispherical masses, separate. They dissolve readily in water, and the solution can be boiled without decomposition. They gradually become dark by exposure to the light, and when heated in the moist state to 212° for any length of time, turn brown. After being dried at the ordinary temperature, they may be kept at 212°. The formula of this salt, whether dried at the ordinary temperature or at 212°, is $C^6 H^6 NO^3, AgO$. It furnished 55·2 per cent. of silver; theory requires 55·1.

Alanine and Oxide of Lead.—Oxide of lead is dissolved in considerable quantity on ebullition with an aqueous solution of alanine. On evaporation and cooling, colourless needles, of a vitreous lustre, crystallize from the solution. In another preparation the aqueous solution was mixed with alcohol. The liquid became turbid, and congealed to a mass of radiately-grouped needles. On drying over sulphuric acid, they were decomposed, with loss of water, into a perfectly white meal, which no longer dissolved entirely in water; the filtered solution had an alkaline reaction, and became turbid on exposure to the air, with separation of carbonate of lead.

Alanine and Baryta.—An aqueous solution of alanine, on boiling with carbonate of baryta, takes up much baryta, and acquires an alkaline reaction. On evaporation, a compound of alanine and baryta separates, which dissolves in water, and imparts to it an alkaline reaction. When a current of carbonic acid is passed through the solution of alanine-baryta for some time, nearly the whole amount of baryta is separated in the form of carbonate of baryta. The precipitate again disappears by long ebullition.

From the preceding experiments, it results that alanine forms compounds with the metallic oxides, in which 1 equiv. metallic oxide replaces 1 equiv. water. They have an alkaline reaction in those cases where the metallic oxide has this reaction.

In many respects the properties of alanine agree with those of glycocoll and leucine; and that of combining both with acids and bases is especially characteristic of these substances. Some time ago Gerhardt and Laurent drew attention to the relation of glycocoll and leucine, already expressed by the formulæ, and at the same time declared sarcosine to be homologous with them. If however homologous bodies are such as differ in their chemical formulæ by $C^n H^n$, and exhibit similar relations of combination and decomposition, the latter statement would appear to be incorrect. Sarcosine has not the property of combining with metallic oxides; and it is rather alanine which should occupy the second place in the series beginning with glycocoll:—

Glycocoll	$C^4 H^5 NO^4$.
Alanine	$C^6 H^7 NO^4$.
Unknown	$C^8 H^9 NO^4$.
Unknown	$C^{10} H^{11} NO^4$.
Leucine	$C^{12} H^{13} NO^4$, &c.

Formerly the compounds of glycocoll and leucine with nitric acid were erroneously regarded as conjugate acids. I have recently

drawn attention to the fact, that the so-called leucino-nitrates, as also the corresponding glycocoll compounds, are simply combinations of leucine or glycocoll with nitrates. This led me to examine whether alanine was in like manner capable of combining with nitrates.

The experiments made with this object did not lead to any satisfactory results. I must leave it undecided for the present, whether alanine forms compounds with nitrates similar to those of glycocoll and leucine. A compound of nitrate of silver with alanine was very easily obtained; but this can scarcely be considered to furnish any proof, as nearly all the organic bases, as well as several other non-basic substances, unite with nitrate of silver. When the mixed solutions of nitrate of silver and excess of alanine are evaporated, a somewhat blackened residue is obtained, which dissolves in alcohol, excepting the excess of alanine. The alcoholic solution deposits, on slow evaporation, tolerably hard, colourless rhombic prisms, which are the compound of alanine and nitrate of silver. When gently heated upon platinum, they melt, give off combustible vapour, and are then decomposed with a slight deflagration, leaving a residue of spongy silver.

I have also obtained, by saturating nitrate of alanine with oxide of copper and evaporation, blue crystals insoluble in alcohol, which appeared to be a compound of nitrate of copper with alanine-oxide of copper, corresponding perhaps to the glycocoll compound analysed by Boussingault, $C^4 H^5 NO^4$, 2CuO, HO, NO^5.

Metamorphoses of Alanine.—I have not been able to examine more minutely the decompositions of alanine from want of material. It is not altered by boiling with acids, as is evident from its mode of preparation. Alanine dissolves in concentrated sulphuric acid, and can be heated to boiling without any blackening or evolution of sulphurous acid. It likewise experiences no change on ebullition with solution of caustic potash; but on evaporating this solution, when the mass has nearly become hydrate of potash, ammonia escapes, and at the same time a lively evolution of hydrogen is perceptible. If the operation is interrupted at this period, and the residue distilled with dilute sulphuric acid, prussic acid passes over with the water along with a volatile acid having a strong acid reaction, and which appears, from its reactions, to be acetic acid. It is known that leucine furnishes, under the same circumstances, the corresponding valerianic acid. Glycocoll gives, according to Horsford's statements, on fusion with potash, cyanide of potassium and oxalate of potash, which latter has originated, at least in part, from the eliminated formic acid.

When an aqueous solution of alanine is heated with peroxide of lead, it is decomposed into carbonic acid, aldehyde and ammonia. When alanine is boiled with dilute sulphuric acid and peroxide of lead, the same products are formed; but the distillate has, in this case, a slight acid reaction, probably owing to the production of some acetic acid from the aldehyde. I was not able to detect any nitrogenous substance in the distillate. Leucine furnishes, with

peroxide of lead, valeronitrile and the aldehyde of butyric acid, so that in this case the decomposition is not quite analogous.

Formation of Lactic Acid from Alanine.—Lactamide, which is isomeric with alanine, is decomposed, according to the observations of Pelouze, into lactic acid and ammonia when it is boiled with dilute acids or alkalies. Alanine, as above stated, experiences no decomposition under similar circumstances. Some time ago I drew attention to the fact, that the action of nitrous acid, first employed by Piria for the preparation of malic acid from asparagine, enables us in many cases to decompose nitrogenous substances, which are not altered by alkalies and acids, in the same manner as true amides. The result of the decomposition may be expressed arithmetically, NH being eliminated from the compound and O^2 assimilated:—

$$NO^3 + C^n H^m NO^p = C^n H^{m-1} O^{p+2} + 2N + HO.$$

I have succeeded in decomposing alanine in this manner. When a current of nitrous acid, evolved from a mixture of starch and nitric acid, and freed as much as possible from nitric acid by being passed through a cold intermediate vessel, is conveyed into an aqueous solution of alanine, a lively disengagement of a colourless gas, nitrogen, is soon observed. It generally contains some nitric oxide, arising from the decomposition of the nitrous acid by water. When the whole of the alanine is decomposed, all the nitrous acid is converted into nitric oxide and nitric acid, so that the evolved gas contains only nitric oxide. The very acid liquid was concentrated at a gentle heat, and the syrupy liquid agitated with æther. The æther floating upon the aqueous solution had dissolved an acid, which remained on the evaporation of the æther as a thick liquid, miscible in every proportion with water and alcohol. This strongly acid and somewhat bitter liquid possessed all the properties of lactic acid; it formed with bases salts which were soluble in water, and gave no precipitate with reagents. I prepared the zinc salt of the acid by boiling with oxide of zinc; it remained on evaporation in crystalline crusts, which presented under the microscope precisely the appearance of the ordinary lactate of zinc. It burnt on being heated upon platinum, diffusing the highly characteristic odour of lactic acid, leaving a residue of oxide of zinc. I confirmed by analysis the identity of the zinc salt prepared from alanine with the lactate of zinc procured from sugar. The following are the results, the salt being dried between 212° and 230°:—

		Calculated.		Found.	
1 equiv. lactate of zinc	121·5	=	81·8		
3 equivs. water of crystallization	27		18·2	18·2	18·3
	148·5		100·0		
Carbon	29·43	6	= 36	29·63	
Hydrogen	4·18	5	5	4·11	
Oxygen	..	5	40	32·93	
Oxide of zinc	33·10	1	40·5	33·33	

The properties and composition of the lactate of zinc, prepared

from alanine, show that it contains the same modification of lactic acid as is produced by the fermentation of sugar. The lactic acid contained in the flesh furnishes, as is well known, with oxide of zinc, a salt which crystallizes with 2 equivs. water of crystallization, and which is far more soluble in water and alcohol than the lactate of zinc prepared by me.

The production of lactic acid from alanine may be represented by the following equation:—

$$\underset{\text{Alanine.}}{C^6 H^7 NO^4} + NO^3 = \underset{\text{Lactic acid.}}{C^6 H^6 O^6} + 2N + HO.$$

This new mode of formation of lactic acid may be regarded as a confirmation of the theory which formed the starting-point for the preceding experiments, viz. that lactic acid is a conjugate compound of formic acid and aldehyde. At all events, I have succeeded in composing from the elements of aldehyde and prussic acid, which latter readily passes into formic acid, lactic acid, just as former experiments had demonstrated the resolution of the conjoined compound into aldehyde, carbonic oxide and water.

If we take into consideration the resemblance of the combining proportions which the individual members of the series of acids ($C^{2n} H^{2n} O^4$), of their alcohols, and of the aldehydes $C^{2n} H^{2n} O^2$, exhibit, then it may be predicted with certainty that the other aldehydes of this series will combine in an analogous manner with prussic acid, and so produce the failing members of the series $C^{2n} H^{2n+1} NO^4$. The experiments of Guckelberger and Tilley have already shown, that in butyral and œnanthal the different metamorphoses, with which we have become more accurately acquainted by the study of the aldehyde of acetic acid, are repeated. These aldehydes are some of them extremely troublesome to prepare in large quantity; others are not yet known; and I have therefore not yet been able to extend the investigation in this direction. It would be highly interesting to treat valeral with prussic acid and muriatic acid, when most probably leucine or an isomeric substance would be formed.

The preceding experiments might also be extended in another direction. Prussic acid may be viewed as the first member of the series $C^{2n} H^{2n-1} N$, which comprises the nitriles of the so-called volatile fatty acids. It is possible that from aldehyde-ammonia and the other nitriles, compounds corresponding to alanine might be obtained. Prussic acid differs however in its behaviour considerably from the other nitriles of the series, so that the production of the members homologous with alanine in this way is less probable.—Liebig's *Annalen*, July 1850.

On some Compounds formed from Cyanuric Acid and Æther. *By* Dr. Limpricht.

The recent investigations of Wöhler* on cyanuric acid have shown that the composition of this acid is expressed by $C^6 N^3 HO^4$,

* Chem. Gaz., vol. v. p. 140.

that consequently 1 atom of hydrogen belongs to its composition, and that it is a bibasic acid. This view has recently been again controverted by M. Wurtz*, owing to the discovery of an æther compound which he obtained by heating a mixture of cyanurate of potash with sulphovinate of potash, and which is of special interest from its having the formula $C^6 N^3 O^3 + 3C^4 H^5 O$; thus apparently confirming the former view of the constitution of cyanuric acid, according to which it is $C^6 N^3 O^3$ and a tribasic acid. Although the correctness of the analytical results found by Wurtz were above all doubt, no facts were to be found in the statements as to the deportment of this body, which justified the assumption that it really was the compound of the tribasic cyanuric acid, $C^6 N^3 O^3$, with 3 equivs. oxide of æthyle. To solve this doubt, I commenced an investigation on the subject, from which I believe I am able to demonstrate that the compound discovered by Wurtz, although it certainly has the quantitative composition ascribed to it by him, contains neither cyanuric acid nor oxide of æthyle, and is therefore not to be considered as the æthyle compound of tribasic cyanuric acid, the existence of which does not refute the view recently advanced respecting the constitution of cyanuric acid.

This is evident, in the first place, from the behaviour of this body towards alkalies. According to all our present experience, the true æthyle compounds are decomposed at the ordinary temperature by alkalies into a salt of the acid contained in it, whilst the æthyle or its oxide makes its appearance as alcohol.

Wurtz himself had found, that, on treating his cyanuric æther with solution of caustic potash, he did not obtain cyanuric acid and alcohol, but carbonic acid and æthylamine. I have confirmed this reaction, and at the same time have observed that the formation of carbonic acid and æthylamine is preceded by the formation of another substance. This is better observed when barytic water is used instead of solution of caustic potash. On ebullition with it, the cyanuric æther takes up 3 equivs. water, parts with 3 equivs. carbonic acid to the baryta, and there remains, after removal of the baryta and evaporation, a turpentine-like body of the composition $C^{15} H^{18} N^3 O^3$. At 338° F. a part distils over unaltered; the other part is decomposed into 1 equiv. æthylamine and another less volatile substance.

$C^{15} H^{18} N^3 O^3$ is resolved into $C^4 H^7 N + C^{11} H^{11} N^2 O^3$.

This decomposition takes place more rapidly at 392°. The solid body exhibits neither acid nor alkaline reaction, and cannot be combined with any other substance. It melts at 223°, and sublimes at about 482°. When boiled with solution of caustic potash, it assimilates water, and is resolved into carbonic acid and æthylamine—

$$C^{11} H^{11} N^2 O^3 + 3HO = 3CO^2 + 2C^4 H^7 N.$$

I have assured myself that the same products are formed with solution of caustic potash; for if the process is interrupted before it is finished, the residue is found to contain both the thick liquid sub-

* Chem. Gaz., vol. vi. p. 195.

stance $C^{15} H^{18} N^3 O^3$ and the crystalline one $C^{11} H^{11} N^2 O^3$. Potash dissolved in absolute alcohol, and added to a similar solution of cyanuric æther, produces after some time, even in the cold, a precipitate of carbonate of potash.

In the course of this investigation, I have discovered several other bodies, which from want of material I have hitherto not been able to examine more closely, although I consumed a quantity of cyanuric acid which had been prepared from at least 6 lbs. of pure urea.

At present I will describe more in detail only one of these substances, which I have examined more minutely, and which stands in close connexion with that discovered by Wurtz. The empirical formula for this body is $C^{14} H^{11} N^3 O^6$, whilst the so-called cyanuric æther of Wurtz is $C^{18} H^{15} N^3 O^6$. If this latter, as is actually admitted by Wurtz, is viewed as $C^6 N^3 O^3 + 3C^4 H^5 O$, the body observed by me might be represented by the composition—

$$C^6 N^3 O^3 + \left\{ \begin{matrix} 2C^4 H^5 O \\ HO. \end{matrix} \right.$$

It is obtained in the preparation of Wurtz's cyanuric æther, and apparently passes over combined with methylamine, on the application of increased heat at the end of the operation, from the mixture of sulphovinate and cyanurate of potash. As this compound does not crystallize, it remains in the mother-ley of the cyanuric æther. It is decomposed on ebullition with barytic water, methylamine escapes, and the new substance crystallizes from the liquid freed from baryta by means of sulphuric acid in beautiful six-sided prisms with three terminal facets; it is pretty soluble in hot water, alcohol and æther; from the two last it crystallizes in obtuse rhombohedrons. The aqueous solution has an acid reaction. It melts at 253°, and can be sublimed unaltered at a higher temperature.

Its weight is not increased either in dry ammoniacal or in muriatic acid gas. It dissolves in ammonia, solution of caustic potash and barytic water more readily than in water, but crystallizes from them with its previous properties. The hot ammoniacal solution, mixed with nitrate of silver, deposits on cooling acicular crystals, having the composition $C^{14} H^{10} N^3 O^5 + AgO$; it likewise furnishes crystalline precipitates with solutions of lead, copper and protoxide of mercury. No combinations with potash and baryta could be obtained, even by accurately decomposing the silver compound with chloride of potassium or chloride of barium.

The lead compound, mixed with sulphovinate of potash and submitted to dry distillation, furnishes the cyanuric æther of Wurtz.

Fused with hydrate of potash, this substance disengages æthylamine.

It is no more possible to separate cyanuric acid or alcohol from this substance than from that discovered by Wurtz, although it might be regarded, as above stated, as $C^6 N^3 O^3 + \begin{matrix} 2C^4 H^5 O \\ HO \end{matrix}$; therefore as a second æther of the tribasic cyanuric acid with 1 equiv.

water instead of the third atom of æther, or as the æther of cyanuric acid, assumed to be bibasic, viz. $C^6 N^3 HO^4 + 2C^4 H^5 O$.

It is impossible to decide at present as to the true constitution of this body, but it seems to me proved that it contains neither cyanuric acid nor oxide of æthyle; its formation at so high a temperature as that at which cyanuric acid and oxide of æthyle always experience a metamorphosis, led *à priori* to the conclusion, that it could no longer contain these compounds as such. It might be compared with the isethionic acid, which appears to be formed from the æther isomeric with the oxide of æthyle, and from which likewise neither æther nor alcohol can be separated.—Liebig's *Annalen*, lxxiv. p. 208.

On Stibæthyle. *By* C. Löwig *and* E. Schweitzer.

[Continued from page 399.]

Constitution of Stibæthyle.—Upon a first view, stibæthyle surprises us by its remarkable capability of combining with the negative elements. If by an organic radical we are to understand in general a definite complex atom of similar or different elements, united in such manner that it acts precisely like an atom of an elementary substance towards other elements, then we know of no body in the whole organic chemistry, excepting kakodyle, which possesses this property in such a degree as stibæthyle. A body which combines directly with the negative elementary principles, partly with the production of fire, which decomposes muriatic acid gas just like potassium, which is separated by potassium from all its compounds furnished with its previous properties, whose oxide unites directly with acids forming salts, whose sulphuret precipitates the metallic salts like sulphuret of potassium, must be regarded as a radical with the same right, notwithstanding its compound nature, as potassium in the corresponding compounds; and even the opponents of the radical theory must confess that it has gained considerably in probability by the discovery of stibæthyle, and by the isolation of methyle, æthyle, amyle, &c.

But another question arises,—How are the individual atoms combined in such a radical? and in answering this question even the defenders of the radical theory may entertain different opinions. In the compounds which stibæthyle forms, it must always be taken as a whole; but if we consider its composition more closely, we are led in the first place to compare it with antimoniuretted hydrogen, in which the hydrogen atoms are replaced by atoms of æthyle. With the same right stibæthyle may be compared with ammonia, the more so, as very recently, compounds have been discovered which form ammonias, in which 1 atom of hydrogen is replaced by 1 atom of methyle, æthyle, amyle. But this analogy disappears on comparing the stibæthyle compounds with those of ammonia; whilst the remarkable bases of Wurtz, as well as the corresponding aniline bases of Hofmann, agree as regards their combining proportions with ammonia. The substitution of aniline for the hydrogen in

ammonia is in favour of the view, that many organic bases, especially those which consist only of carbon, hydrogen and nitrogen, like aniline, toluidine, &c., contain neither ammonia nor amidogen, but represent, like ammonia, peculiar hydrogen bases, which behave like ammonia as to their combining proportions. Ammonia, methylamine, ethylamine, amilamine, as also the corresponding aniline bases, do not combine with oxygen, sulphur, or the halogens, unless 1 atom of hydrogen has been assimilated, and these compounds contain 1 atom of the above-mentioned elements to 1 atom of base. Stibæthyle, on the contrary, unites directly with them, and behaves in this respect, as well as in its action upon the hydracids, exactly like a strongly-positive metal, only the stibæthyle always unites with 2 atoms of the non-metallic element, whilst for instance only 1 atom is contained in the corresponding potassium compounds, with which those of stibæthyle entirely agree. In this respect it likewise differs from kakodyle, which it otherwise greatly resembles, for the principal series of compounds of kakodyle comparable with those of stibæthyle contains 1 atom of oxygen, sulphur, &c. to 1 atom of kakodyle. As is well known, Kolbe regards kakodyle as a combination of 2 atoms of methyle to 1 atom of arsenic; a view, the correctness of which can scarcely be doubted. According to Kolbe, kakodyle is a radical in which 2 atoms of methyle are conjoined with 1 atom of arsenic; and he finds in it an essential support for his theory on the composition of the organic acids of the dyhenyle series; thus, for instance, according to Kolbe, acetyle is a radical which consists of 1 atom of methyle conjoined with 2 atoms of carbon. According to this view, the arsenic determines the combining capacity of the kakodyle; the arsenic unites with oxygen, sulphur, chlorine, &c., and the conjoined methyle enters as such into all the compounds. The oxide of kakodyle is therefore $(C^2 H^3)^2, AsO$; kakodylic acid corresponds to the formula $(C^2 H^3)^2, AsO^3$; and in perfect analogy with this, acetic acid is methyle conjoined with oxalic acid, and its formula is therefore $(C^2 H^3) C^2 O^3$. According to this theory, which is also supported by other facts, the conjoined methyle acts quite an indifferent part in the above-named compounds. The compounds of stibæthyle induced the authors to oppose the following theory to that of Kolbe:—Kakodyle is a radical consisting of MeAs conjoined with 1 atom of methyle, and its rational formula accordingly becomes (MeAs)Me; its combining capacity is determined therefore by the free atom of methyle, and not by the arsenic. The oxide of kakodyle answers therefore to the protoxide of manganese, and the kakodylic acid to manganic acid. In the same way stibæthyle consists of 2 atoms of æthyle united with the conjunct AeSt; consequently its formula is (AeSt), Ae^2. The reason why stibæthyle takes up 2 atoms of sulphur, &c. is owing to the 2 atoms of free æthyle which are conjoined with AeSt. If these 2 atoms separate, there still remains the conjunct æthylestibyle, which now appears as a radical; the positive character of the compound disappears in the same proportion, the antimony is the determining element, and consequently the æthylestibyle unites with 5 atoms of

oxygen, sulphur, &c. Were we to succeed in oxidizing the stibæthyle still higher, a bibasic acid would undoubtedly be formed. This theory explains very simply and naturally the similar and dissimilar behaviour between kakodyle and stibæthyle.

Hitherto Frankland has not stated whether the radicals methyle, æthyle, amyle, isolated by him, furnished the same compounds which are already known as methyle-, æthyle- and amyle-compounds; it is however evident from his statements, that their combining capacity is not comparable with that of the methyle in kakodyle, and of æthyle in stibæthyle, as they appear to be indifferent. This difference is not surprising; these radicals behave in the isolated state like many of the elementary bodies, which only unite with other bodies at the moment of their liberation from existing combinations, in which state they have not yet assumed their physical properties. The methyle and æthyle in kakodyle and stibæthyle are in the same condition as the elements at the moment of their liberation, whence arises their great affinity.

The question now presents itself,—Can the view which the authors have propounded respecting the constitution of kakodyle and stibæthyle be likewise extended to the radicals on which are based the formic, acetic, and the dyhenyle acids generally, *i. e.* can, for instance, acetyle be viewed as a radical consisting of 2 atoms of carbon conjoined with 1 atom of methyle $=C^2, C^2H^3$, or must we admit with Kolbe methyle to be the conjunct?

The authors consider as most probable that acetyle $=C^4H^3$ and æthyle $=C^4H^5$, and that a subdivision into C^2 and C^2H^3 is produced by electrolytic or some other action. According to Kolbe, acetic acid is methyle-oxalic acid; when acetate of ammonia is distilled with anhydrous phosphoric acid, the same compound is obtained as by the action of cyanogen upon methyle. If this substance is cyanide of methyle, as has been generally supposed, its formation from acetate of ammonia is explained in a very simple manner. Oxalic acid and ammonia form water and cyanogen, which latter unites with the conjoined methyle; and it is precisely on the formation of cyanide of methyle from acetate of ammonia that Kolbe essentially bases his theory. But this body may likewise be viewed as a combination of nitrogen with acetyle, and at least as many valid reasons may be advanced in favour of this view as for the formula MeCy. In the first place, its perfect indifference on the living organism; a body which in certain respects represents prussic acid, viz. prussic acid in which H is replaced by methyle, would certainly exhibit poisonous properties. The great tendency to decomposition of cyanogen speaks in favour of the production of nitruret of acetyle; further, the production of formiate of ammonia from aqueous prussic acid; these at least are as favourable to the one view as the formation of prussic acid from formiate of ammonia is to the other. The few experiments which have been made with cyanide of stibæthyle are highly favourable to such a transformation. Perhaps the following experiments, made long since by the authors, may contribute somewhat to decide this question.

When an intimate mixture of 2 parts of perfectly anhydrous acetate of lead with 1 part of equally dry Paris blue is submitted to a gentle heat in a retort, a lively disengagement of gas very soon results; a mixture of about 2 vols. of carbonic acid gas to 1 of carbonic oxide escapes, whilst at the same time a colourless ætherial liquid collects in the receiver. When the liquid distillate, which passes over at a moderate heat, is removed, and the temperature is then gradually raised until the retort becomes red-hot, a yellow oily product distils over, and at the same time, especially towards the end of the operation, a large quantity of carbonate of ammonia is given off. The residue consists of a pulverulent mixture, which is extremely pyrophoric, and for several days continues to liberate ammonia in large quantity when exposed to moist air. The above-mentioned liquid product, which distils over at the commencement, is colourless, and possesses a faint ammoniacal odour, which is not disagreeable, has a sweetish taste, and mixes with water, æthyle and alcohol in every proportion. From the aqueous solution the compound is again completely separated by chloride of calcium or caustic potash. To expel the ammonia, the distillate was shaken with some phosphoric acid, then rectified over peroxide of mercury and dehydrated by chloride of calcium. Thus purified, the product is perfectly colourless, very liquid, of an agreeable ætherial odour and a sweetish burning taste. It burns with a bright luminous flame, and has a specific gravity of 0·790 at 59°. When it is heated in the water-bath, it begins to boil at 156°; the boiling-point however quickly rises to 160°, then remains stationary for some time, but soon rises to 176°, at which temperature the greater portion passes over; the last portions distil over however only at 181°.

The analyses of the distillate which passed over at 160° furnished results which may be reduced to the formula $C^{10}NH^9O^2$:—

Carbon	60·40	60·17	10 =	60	60·60
Hydrogen	9·56	9·79	9	9	9·10
Nitrogen	14·72	13·11	1	14	14·14
Oxygen	15·32	16·73	2	16	16·16

The distillate obtained at 176° gave results which agree with the formula C^7H^6NO:—

Carbon	59·83	60·26	7 =	42	60·00
Hydrogen	8·74	8·37	6	6	8·57
Nitrogen	20·58	..	1	14	20·00
Oxygen	10·58	..	1	8	11·43

One analysis of the distillate which had passed over at 171° furnished,—C 60·23, H 8·92 and N 18·42 per cent.

Of the liquid which distilled over at 181° too little was obtained for analysis. It may however be admitted that the quantity of nitrogen in it was still greater.

The different distillates agree perfectly with each other in their chemical and physical relations. When agitated with solution of caustic potash, no action is perceptible in the cold; but on the appli-

cation of heat, ammonia escapes in abundance. If, when no further evolution of ammonia occurs, the residue is distilled with an excess of phosphoric acid, acetic acid passes over. If some potassium be dissolved in absolute alcohol, a solution of anhydrous potash in absolute alcohol is obtained; now this acts neither in the cold nor on the application of heat upon the substances; but if only a few drops of water are added, ammonia is instantly disengaged. Potassium acts with violence upon the substances with an abundant formation of cyanide of potassium. Acids cause no perceptible decomposition in the cold; but if the product be boiled with dilute sulphuric acid, acetic acid distils over, and the residue contains sulphate of ammonia.

The same reactions are likewise observed in the decomposition of the nitruret of acetyle or of the so-called cyanide of methyle; now $C^{10}NH^9O^2 - NC^4H^3 = C^6H^6O^2$ and $NC^7H^6O - NC^4H^3 = C^3H^3O$. The substance which passed over at 160° contains consequently 2 atoms, and that at 176° 1 atom of acetone and 1 atom of nitruret of acetyle or cyanide of methyle. Although it might be suspected that a mixture of the two bodies would begin to boil below 158°, and that consequently on analysis it would scarcely furnish a definite atomic proportion, the authors do not consider it to be a chemical compound, from the specific vapour of the liquid boiling at 176° being opposed to any such view; they obtained the following results:—

Excess in weight of the balloon filled with vapour over that filled with air	0·092 grm.
Capacity of the balloon	256 cub. centim.
Residue of air	0
Temperature of the atmosphere	73°·4
Temperature of vapour	212°
Height of the barometer	735 millims.
Specific gravity of the vapour	1·60

		spec. grav.
7 measures of	carbon	5·8520
12 ...	hydrogen	0·8316
2 ...	nitrogen	1·9412
1 ...	oxygen	1·1093
6 measures of gas		9·7341 consequently 1M = 1·622,

or

measures.	spec. grav.		measures.	spec. grav.
C^4H^3	= 2 = 3·7598	and C^3H^3	= 2 = 2·9238	
N	= 2 = 1·9412		O	= 1 = 1·1093
C^4H^3N	= 4 = 5·7010		C^3H^3O	= 2 = 4·0331

A chemical compound would have given, in accordance with all known facts, only 4 measures of vapour. But be that as it may, it is indifferent as regards the present question whether it be assumed to be a chemical compound or a mere mixture. The question is, Can cyanide of methyle be formed in the above decomposition?

That prussian blue is decomposed at a high temperature without disengagement of cyanogen, and that it acts in these circumstances as a reducing agent when heated to redness with metallic oxides, are well-known facts. The formation of cyanide of methyle would presuppose that the nitrogen eliminated on the decomposition of the prussian blue combined with the 2 atoms of carbon with which the methyle is conjoined in the acetic acid to form cyanogen, whilst the carbon of the cyanogen has a reducing action, and that consequently cyanogen is reproduced at the same moment that it is decomposed. Or it must be assumed that the conjoined carbon in the acetic acid has a reducing action, an assumption however which is untenable, because no cyanogen is liberated by heating prussian blue. On the other hand, the explanation is very simple supposing the product to be nitruret of acetyle. The carbon of the cyanogen reduces the acetate of lead; acetyle is set free, which at the moment of its separation combines with the nitrogen of the cyanogen—

$$PbO, C^4 H^3 O^3 + NC^2 = 2CO^2 + C^4 H^3 N.$$

It is true the formation of nitruret of acetyle does not refute the theory advanced by Kolbe. If, for instance, we denote acetyle by $(C^2 H^3) C^2$, it unites as a whole with nitrogen. The formula of the compound is then $N + (C^2 H^3) C^2$, and not $C^2 H^3, Cy$. It appears however that it accords better with facts to consider acetyle as a direct compound of $C^4 H^3$.

The authors have likewise obtained a similar compound of bismuth; it is produced very easily in the action of iodide of æthyle upon the amalgam of bismuth and potassium. Phosphorus likewise furnishes an analogous compound.—*Mith. der Naturforsch. Gesellsch. zu Zurich*, 1850, pp. 1–35.

On the Occurrence of Succinic Acid in the Human Body. *By* Dr. W. Heintz.

In a previous paper*, the author stated that he had obtained from the contents of the hydatid cysts (*Echinococci*) an acid which was probably succinic acid. He has since ascertained by analysis that the acid obtained from the liquid of the hydatids is in reality succinic acid.—Poggendorff's *Annalen*, lxxx. p. 114.

ANALYTICAL CHEMISTRY.

On the Estimation of Oxalic Acid, and on its Separation from Phosphoric Acid. *By* Prof. H. Rose.

Oxalic acid is usually precipitated from solutions of its soluble salts as oxalate of lime. But as the amount of water in this precipitate varies with the temperature, it is usual to convert it by ignition into carbonate of lime, from the weight of which that of the

* Chem. Gaz., vol. vii. p. 477.

oxalic acid can be determined. Insoluble compounds of oxalic acid, as for instance the oxalate of lime, may be decomposed by ebullition with a solution of carbonate of potash or soda, upon which, after separating the carbonate of lime, and saturating the filtered liquid with an acid, the oxalic acid can be again precipitated as oxalate of lime.

In general, however, lime can be more accurately precipitated and determined by oxalic acid than oxalic acid by a solution of a salt of lime. The circumstance that in the precipitation of the oxalic acid an excess of lime-salt is used, and the liquid generally supersaturated with ammonia, renders caution necessary, in order that the precipitated oxalate of lime may not be contaminated with carbonate. But further, the oxalate of lime has a tendency to combine with small quantities of the lime-salt used for the precipitation. Long ago Fritzsche described a double salt of oxalate of lime and chloride of calcium; it is decomposed by water, it is true, but even after long washing, a small quantity of chloride of calcium remains in the oxalate of lime; and on dissolving this in dilute nitric acid, the solution is rendered turbid, although only in a slight degree, by nitrate of silver. When therefore oxalate of lime is decomposed by ebullition with a solution of alkaline carbonate, the liquid separated from the carbonate of lime, supersaturated with hydrochloric acid, and after the expulsion of the carbonic acid mixed with an excess of ammonia and chloride of calcium, the correct amount of carbonate of lime which should be obtained is found, but a slight excess of oxalate of lime.

A far better result is obtained when the solution containing the oxalate and excess of carbonate alkali is rendered slightly acid by acetic acid; and, after expulsion of the carbonic acid, is precipitated with chloride of calcium without being previously saturated with ammonia. But the most accurate method of estimating oxalic acid, both in those compounds which are soluble as well as in those that are insoluble in water, is by the reduction of gold from its chloride. Its amount can be very accurately ascertained, even when it is combined with other acids, from which it is otherwise difficult to separate, for instance phosphoric acid. Both these acids occur in guano.

The reduction of gold from a solution of the chloride proceeds easily and quickly when the solution of the oxalates contains none or but little free hydrochloric acid. But if much free hydrochloric acid is present, not a trace of gold can be reduced from concentrated solutions even by long-continued boiling. This happens only after the whole has been diluted with a large amount of water; and even then long boiling is necessary to ensure the complete reduction of the gold. Neither sulphuric nor phosphoric acid exerts any similar action to the hydrochloric acid; for even in the presence of pretty considerable quantities of those acids, the gold is reduced from concentrated solutions, especially when the whole is heated to boiling.

Already Berzelius employed a solution of gold to check the composition of oxalic acid after Pelletier had drawn attention to the decomposition of oxalic acid by a gold solution. Since then oxalic

acid has been frequently used to determine the amount of gold in solutions, especially when they contained other metals upon which oxalic acid has no reducing action. But, on the other hand, a solution of gold can be employed, with the same advantage, for estimating oxalic acid with accuracy in the presence of many other acids.

M. Weber treated a solution of 1·830 grm. neutral oxalate of potash and 2·170 crystallized phosphate of soda ($2NaO+HO+PO^5$), with a solution of sodio-chloride of gold in excess. The neutral oxide of potash furnished on ignition 73·98 per cent. of carbonate; it contains therefore 11·06 per cent. water, which corresponds to more than 1 atom. The phosphate, which did not contain the usual amount of water, left on ignition 49·40 per cent. pyrophosphate of soda. The reduction of the gold began after a few minutes; it was collected after twenty-four hours upon a filter, and weighed 1·320 grm., which corresponds to 0·725 grm. oxalic acid; the salt employed contained 0·706 grm. The difference undoubtedly arises from the oxalate of potash containing more oxalic acid than was estimated from the amount of carbonate of potash it furnished. In the liquid separated from the reduced gold, the gold in solution was removed by oxalic acid, and the phosphoric acid then precipitated as ammonio-phosphate of magnesia. 0·904 grm., $2MgO, PO^5$, was obtained on ignition, which corresponds to 0·573 phosphoric acid. The phosphate employed contained 0·572 grm. phosphoric acid.

In another experiment, M. Weber employed 1·015 grm. oxalate of lime and 0·729 calcined phosphate of lime ($2CaO, PO^5$), which were both dissolved in hydrochloric acid. The oxalate of lime contained 0·494 grm. oxalic acid, which was ascertained by calcining another portion of it. The solution of the salts was boiled for a long time with an excess of sodio-chloride of gold without the slightest reduction being effected. After the whole had been diluted with about five times its bulk of water, the boiling was continued in a flask, and 0·897 grm. reduced gold obtained. This corresponds to 0·492 grm. oxalic acid, and comes very closely to the calculated amount. The gold was removed by sulphuretted hydrogen from the filtered liquid, which was then concentrated, and the lime precipitated by sulphuric acid and alcohol. The alcohol was expelled from the filtered liquid by evaporation, and the phosphoric acid separated as ammonio-phosphate of magnesia. On ignition, 0·660 grm. $2MgO, PO^5$ was obtained, corresponding to 0·418 phosphoric acid; the phosphate of lime employed contained 0·408; the phosphate of magnesia obtained contained a slight trace of lime.—Poggendorff's *Annalen*, 1850, No. viii.

On the Action of Strontia before the Blowpipe.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Dear Sir,—Having just observed in the 'Annuaire de Chimie' for the present year, some statements* by Dr. Muspratt, relative to

* Quoted from the Ann. der Chem. und Pharm., lxxii. p. 118.

the action of strontia before the blowpipe, which reflect more than indirectly upon the accuracy of a little test announced by me in the 'Chemical Gazette' for May 1, 1848 (No. cxxxiii.), I beg in self-defence, although in no uncourteous spirit, to offer a few remarks upon the same.

My test was for the purpose of distinguishing strontia from lithia by fusing the assay-substance with chloride of barium, when I showed that the strontia-flame would be entirely destroyed, as previously observed by Plattner; whilst the red flame produced by lithia *per se* would remain unaffected, or would be actually increased in intensity. Now Dr. Muspratt is made in the *loc. cit.* to state, that in a mixture of equal parts of chloride of barium and chloride of strontium the strontia-flame is alone visible; and again, that this "crimson coloration," as produced by a salt of strontia, is not affected by the addition of chloride of barium unless soda be present; the least trace of the latter, according to his account, being sufficient to destroy the characteristic red tint. To these observations I must reply, that chloride of barium, in much smaller quantity than 50 per cent., entirely prevents the strontia-flame from being rendered visible; and secondly, that the accidental presence of soda can have nothing to do with this reaction, because if we make a mixture of even equal parts of chloride of barium and carbonate of soda, and expose the mass before the blowpipe on a loop of platinum wire, the yellow flame, derived from the soda, will only prevail for a few minutes, and will then give place to the pale green flame of baryta, the whole of the soda being got rid of by rapid volatilization under the form of NaCl. In like manner a mixture of chloride of strontium and carbonate of soda will give, after a well-continued blast, the characteristic crimson flame of the former. I am not aware that this fact has been hitherto pointed out; but that the effect is produced I shall be happy to prove to any one who will take the trouble to call at my office, No. 52 Frith Street.

Dr. Muspratt states furthermore, that only the hydrated and soluble salts of strontia colour the flame *per se*; and that no coloration is effected by the sulphate, phosphate or carbonate. From numerous trials, however, I can safely assert, that both the natural sulphate and carbonate—the celestine and strontianite—produce *per se* a well-marked crimson coloration, if not on the first application of the flame, at least after blowing for a few instants. It is true that with previously-ignited chloride of strontium the flame is at first scarcely coloured; but if the fused bead be shaken from the loop, and the platinum wire be again presented to the flame, the coloration is most intense and persistent; a phænomenon not easily explained, unless it be that the heat required to produce the reaction without the presence of water can scarcely be attained with the larger globule.

I am, dear Sir,
Very truly yours,
EDWARD CHAPMAN,
Professor of Mineralogy in Univ. Coll., London.

THE CHEMICAL GAZETTE.

No. CXCIV.—November 15, 1850.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Amount of Water in Cholesterine and the Products of its Distillation. *By* Dr. W. Heintz.

The author has examined cholesterine as to the amount of its water and the products of its distillation. The material for the investigation was obtained from gall-stones, and purified in the usual manner. An analysis made with the cholesterine thus obtained gave—

Carbon	83·85	28	84·00
Hydrogen	12·00	24	12·00
Oxygen	4·15	1	4·00

The author determined the amount of water in cholesterine. He did not find Schwendler and Meissner's statement of 2·9 per cent. to be correct. His results agree rather with the earlier statements of Pleischl, Kuhn, Gmelin, and a recent determination of Couerbe, who find that crystallized cholesterine loses in the water-bath 5·2–5·4 per cent. of water.

Cholesterine crystallized from alcohol which had lain for three months in the air lost, at 248°, 4·62 per cent. Another sample, which had been first dried over sulphuric acid and then at 266°, contained 5·38 per cent. of water. Cholesterine, which the author crystallized from a mixture of æther and alcohol, following the directions of Schwendler and Meissner, gave, on being heated to 257°, 4·96 and 4·94 per cent. of water. Cholesterine which the author crystallized from recently-prepared absolute alcohol lost on desiccation 5·33 per cent. of water.

The reason why Schwendler and Meissner found so low an amount of water is owing to their having dried the cholesterine over chloride of calcium, and regarded the loss which ensued as hygroscopic water, whilst in reality it was in part water of crystallization.

According to Schwendler and Meissner, the formula of cholesterine is $C^{54}\,H^{72}\,O^{3}+2HO$. But since the amount of water admitted by these two chemists is not correctly determined, it can no longer serve as basis for fixing the formula. According to the analyses of different chemists, the most simple formula for anhydrous cholesterine is $C^{28}\,H^{24}\,O$. If, in accordance with this, we adopt for the hydrated substance the formula $C^{28}\,H^{24}\,O+HO$, theory gives 4·31 per cent. of water, the numbers found by the author were 4·62–5·75, and for cholesterine which had been dried in the air in the pow-

dered state, 4·62, 4·96, 4·94. These last numbers agree sufficiently well with the calculated ones. Moreover, the origin of the three hydrocarbons (with the composition $C^{28}H^{28}$), obtained by Zwenger* on treating cholesterine with sulphuric and phosphoric acids, is well explained from the composition $C^{28}H^{24}O + HO$.

At an elevated temperature cholesterine behaves very differently, according as the heat is quickly increased or kept low. At the temperature of boiling mercury cholesterine distils over unaltered, not merely *in vacuo*, as observed by Chevreul, but likewise with access of air, although very slowly. At first it parts with the chemically-combined water, some of which escapes in the form of gas bubbles only when it is partially fused. If, after the water has been removed, the temperature is increased to near the boiling-point of mercury, and maintained at this point, the cholesterine gradually assumes the gaseous state, but forms white vapours where the temperature is not sufficiently high to retain it in the gaseous state, and again becomes liquid, and finally solid.

When the experiment is made in a retort, its entire space is filled with fumes; and if the experiment is made so that the whole body of the retort has been heated to the boiling-point of mercury, the cholesterine collects in the neck as a fine light white snow, which melts where the temperature is above 278°. The distillate obtained in this manner consists almost entirely of anhydrous cholesterine, which has the smell of some adherent product of decomposition.

The distilled cholesterine had, after recrystallization from alcohol, the same composition as originally; the analysis gave 5·03 per cent. water, and the dry substance furnished—

Carbon	83·89	28	84·00
Hydrogen	12·19	24	12·00
Oxygen	3·92	1	4·00

In the distillation of cholesterine at a higher temperature, at first some impure cholesterine passes over; then follows a mixture of a little cholesterine and likewise a very little α-cholesterone along with the products of distillation; lastly, a thick clear oil, from which by fractional distillation a very liquid hydrocarbon can be separated. The principal mass however consists of a thickish liquid, which quickly absorbs oxygen, and is probably constituted according to the formula $C^{28}H^{22}$. In the distillation the residue in the retort gradually becomes richer in carbon and poorer in hydrogen. It contains no more cholesterine. When the greater portion of the substance has been distilled over, it contains a brown substance, very rich in carbon and sparingly soluble in æther, which contains only 4·5 per cent. of hydrogen, and consists probably of C^3H.

When cholesterine, which has been deprived of its water by fusion, is heated quickly to ebullition over the naked fire, so that only the part of the retort with which the cholesterine is in contact is touched by the flame, three distinct periods are observed. At the commencement a rather considerable amount of undecomposed cholesterine passes over, but mixed with some of its products of de-

* Chem. Gaz., vol. vii. p. 250.

composition. This is apparent from the rapidity with which the distillate solidifies to a crystalline mass. That which next passes over resembles turpentine, is opake, and contains along with the ultimate products of distillation a little cholesterine and a crystalline substance. Lastly, a transparent oily liquid passes over. The distillate contains some water, which is not water of crystallization, but produced by decomposition. At first no gas is formed; a little is disengaged just towards the end of the distillation, when carbon has already begun to separate.

The last product of the distillation, the oil, was thick and yellowish; it was exhausted with boiling alcohol, with a view to separate it into different bodies, but without success. The alcohol took up a portion of the oil along with some cholesterine; what remained undissolved was again boiled with alcohol, and the oil which separated on cooling employed for the analyses I. and II., and that which was left on evaporating the alcoholic solution used for III. and IV. The portion which remained undissolved in alcohol was taken for analysis V. The results of these different analyses are—

	I.	II.	III.	IV.	V.
Carbon	86·67	86·42	86·35	86·99	86·21
Hydrogen ..	12·25	12·22	11·91	11·81	12·37
Oxygen	1·08	1·36	1·74	1·20	1·42

The residue in the retort after the distillation was of a brown colour, and solidified on cooling to a brittle friable mass, which melted at 230°. It was not possible to separate it by æther and alcohol into different substances. It was dissolved in æther, in which it was entirely soluble, and the solution first precipitated with a little, and then with more alcohol. The two products thus obtained furnished on analysis the following numbers:—

	I.	II.
Carbon	86·75	86·80
Hydrogen	11·07	11·13
Oxygen	2·18	2·07

The oily body obtained in the distillation of cholesterine gradually acquired a violet colour by exposure to the air, evidently owing to the absorption of oxygen. As the above experiments to decompose it into different bodies had failed, it was tried to separate the oil by fractional distillation, with the exclusion of the oxygen of the atmosphere. A fresh quantity of oil was prepared from the residue of the previous distillation, and a current of carbonic acid passed over it while it was being heated. The last portion of the distillate was placed in a stoppered bottle with dry chloride of calcium, and well-shaken with it, in order to remove the water formed in the distillation, upon which it was submitted to fractional distillation in a current of carbonic acid.

The rectified oil, after being dried over chloride of calcium, was colourless, very liquid, possessed the odour of the products of distillations of cholesterine in the highest degree, and was not altered by exposure to the air. It began to pass over at 212° very slowly.

which was even the case at 284°. It follows from the rising of the boiling-point that the substance is not a simple one, whilst the elementary analysis proved that it consisted of hydrocarbons of the same relative proportions as in olefiant gas. It gave—

Carbon	85·70	1	85·71
Hydrogen	14·36	1	14·29

The second portion, which was obtained between 284°–464°, was not so liquid, yellowish, became violet in the air, and finally brownish-yellow, and its composition differed considerably from that above-mentioned. It furnished—

Carbon	87·30	28	87·96
Hydrogen	12·46	23	12·04

In experiments subsequently made the author could not again obtain this substance. The product which succeeds it at a higher temperature was a thick oily body, which could no longer be regarded as a pure substance.

It has already been stated that the residue from the distillation of cholesterine gave 86·8 per cent. of carbon and 11·1 per cent. of hydrogen. After this residue had again been distilled in a current of carbonic acid, the following results were obtained:—

	I.	II.	III.
Carbon	87·82	84·76	87·90
Hydrogen	10·85	..	10·68
Oxygen	1·33	..	1·42

which show that in the second distillation the portion of cholesterine which did not distil over is deprived of hydrogen and oxygen, but not in the proportion in which they form water. The amount of hydrogen separated from it is much greater in comparison to the amount of oxygen removed than corresponds to this proportion. This explains why, in the decomposition of cholesterine by heat, a hydrocarbon is formed consisting of equal atoms of carbon and hydrogen, whilst cholesterine itself contains only 24 atoms hydrogen to 28 atoms carbon.

A second series of experiments on the products of distillation of cholesterine were made with perfectly fresh material. As before, water and cholesterine first made their appearance, then came the above-mentioned turpentine-like mass; and on distilling at a great heat, a thick liquid yellowish oil, which became brown in the air, was obtained. This oil was now freed from water, and submitted to fractional distillation. The first fraction, which passed over at 284°, after being rectified possessed the properties of the first distillate, which had been obtained from the products of the distillation-residue of the cholesterine. The composition agreed perfectly with that of that product, viz.

Carbon	85·52	1	85·71
Hydrogen	14·25	1	14·29

The residue of this distillation was somewhat thicker than the previously-analysed product, but nevertheless possessed the same odour;

and after it had been heated at a lower temperature (about 308°) in a current of carbonic acid, a small quantity of a thick oil remained. It exhibited on analysis the composition—

Carbon	86·23
Hydrogen	13·05
Loss (oxygen)	0·72

The second fraction, which had been obtained last in the distillation of cholesterine in a current of carbonic acid at 284°, was a pale yellowish thickish oil, which turned brownish-yellow in the air, and became almost like turpentine. It had the composition—

Carbon	87·83	28	88·42
Hydrogen	11·48	22	11·58

After this oil had stood for some time exposed to the air, the composition was altered. Two portions, distilled one after the other, had the following composition:—

Carbon	87·24	87·34
Hydrogen	11·11	11·11
Oxygen	1·65	1·55

Judging from these results, the substance had absorbed oxygen, but had parted with hydrogen. Probably the product of distillation of cholesterine was a pure hydrocarbon of the formula $C^{28}H^{20}$, which had absorbed oxygen from the air.

Further experiments on the first more volatile and the above-described second products agree insofar with what has been above stated, that the first is a hydrocarbon consisting of equal equivalents of carbon and hydrogen; and the second, the preparation of which in a pure state is very difficult, is a hydrocarbon of the formula $C^{28}H^{22}$, which changes very easily with access of air. From all these experiments it follows that cholesterine on dry distillation is decomposed with loss of water into substances containing more oxygen and less hydrogen. But these latter cannot be prepared free from oxygen by mere distillation, as they all (or perhaps only one of them) hold it firmly combined.

When the distillation of cholesterine is carried on until about $\frac{1}{10}$–$\frac{1}{12}$ of the quantity employed is left in the retort, a substance is formed which contains much less hydrogen in proportion to the carbon than cholesterine itself. The formation of the volatile substance consisting of equal atoms of carbon and hydrogen, may possibly find an explanation in this circumstance. It is likewise easy to perceive that after the greater portion has passed over, the residue again furnishes the above hydrocarbon on the renewed application of heat.

Lastly, the author examined the products which are formed on passing vapour of cholesterine through an incandescent tube. A tarry mass and much gas were obtained. The gas burnt with a bright blue flame, yellowish at the point, which however did not give much light, did not decrease in volume by agitation with hydrate of potash, contained therefore no carbonic acid, and must consequently

have been the two hydrocarbons, hydrogen and carbonic oxide. The analysis of this gas showed that it consisted of 78·93 carbon and 21·07 hydrogen, being a mixture of marsh gas and olefiant gas.

It has already been observed, that in the distillation of cholesterine, besides the products hitherto described, was a thick turpentine-like mass, which formed the second distillate. This product contained much cholesterine, and appears indeed to have consisted merely of a mixture of this with a small quantity of the α-cholesterone of Zwenger.

In conclusion, the author observes, with respect to the formulæ of cholesterine, that $C^{28} H^{24} O + HO$ is the most probable.—Poggendorff's *Annalen*, lxxix. p. 524.

On some Salts of Arsenious Acid. *By* JAMES STEIN.

The arsenites with alkaline base are soluble in every proportion in water; those of the alkaline earths are but sparingly soluble in water, but readily in acids and in alkalies; and those of the heavy metallic oxides are insoluble in water, but easily soluble in alcohol and in æther. The salts generally contain water, of which only a portion is expelled at 212°.

Arsenite of Ammonia, $2NH^3 O, AsO^3$, is obtained by the action of concentrated aqueous ammonia upon arsenious acid in small crystals, which are rinsed with alcohol or æther, in which they are insoluble. They are rapidly decomposed by exposure to the air, parting with the whole of the ammonia. For analysis, the salt was prepared with an excess of ammonia, and rinsed with æther. It was then dried by pressure between folds of bibulous paper, and weighed in dilute muriatic acid in order to avoid a loss of ammonia. The arsenious acid was precipitated from the solution by sulphuretted hydrogen, and the ammonia in the filtered solution determined in the form of ammonio-chloride of platinum. Its composition is—

Arsenious acid.....	65·15	1 =	99	65·56
Ammonia.....	34·85	2	52	34·44

The solution of this salt, mixed with a slight excess of arsenious acid in order to avoid the presence of any free ammonia, was used for the preparation of some insoluble salts by double decomposition. Pasteur has described a salt which agrees with the preceding one.

Arsenite of Baryta.—When barytic water is added to a solution of arsenious acid until no further precipitate results, arsenite of baryta falls as a white flocculent mass. The addition of alcohol increases the amount of the precipitate. The salt was collected on a filter and washed with dilute alcohol, in which however it is somewhat soluble. After desiccation over sulphuric acid, the formula of the salt is $2BaO\ AsO^3 + 4HO$. 2 equivs. water are expelled at 212°, the remainder at a higher temperature, when at the same time metallic arsenic sublimes, whilst the residue contains arseniate of baryta. For analysis, the salt was heated with muriatic acid with the addition of chlorate of potash, the baryta precipitated by sulphuric acid, and the arsenious acid then determined in the form of

ammonio-arseniate of magnesia. The amount of water was found by the loss. The following are the results obtained:—

Baryta.....	53·35	2 =	153·4	53·15
Arsenious acid	34·57	1	99	34·35
Water.....	12·08	4	36	12·50

Arsenite of Strontia.—An aqueous solution of arsenious acid produces in strontian water no precipitate; but the arsenite of ammonia causes a white flocculent precipitate in solutions of salts of strontia, the quantity of which is increased upon the addition of alcohol. This salt is pretty soluble in water, and is obtained, on evaporating the aqueous solution, as a fine crystalline powder. The salt, after being washed in the same manner as the preceding one, and dried over sulphuric acid, possessed the formula SrO, AsO^3+4HO. At 212° it loses 1 equiv. water, and at a higher temperature is decomposed like the baryta salt. For analysis, the salt was dissolved in dilute muriatic acid, the arsenious acid precipitated by sulphuretted hydrogen, the precipitate with the filter dissolved in *aqua regia*, and the arsenic acid precipitated by the addition of solution of magnesia and ammonia. The strontia was determined as sulphate:—

Strontia	29·22	1 =	52	27·82
Arsenious acid.....	51·45	1	99	52·94
Water	19·33	4	36	19·24

Arsenite of Lime.—On precipitating arsenious acid with excess of lime-water, there is probably obtained a mixture of two salts. The analyses of the precipitate, when calculated according to the formula $2CaO, AsO^3$, give an excess of lime, which points to an admixture of $3CaO, AsO^3$. It dissolves in an excess of arsenious acid; and when there is not sufficient to dissolve it, a salt remains, the composition of which, after being dried over sulphuric acid, may be represented by $3CaO, 2AsO^3+3HO$. At 212° it loses 1 equiv. water, and is decomposed on ignition like the previous salt. The following are the analytical results:—

Lime.....	26·1	3 =	84	27·2
Arsenious acid.....	65·7	2	198	64·1
Water	8·2	3	27	8·7

Arsenite of Magnesia.—When solutions of sulphate of magnesia and arsenite of ammonia are mixed, several days elapse before any precipitate is produced. When free ammonia is present, a copious precipitate is immediately produced, which I obtained free from an admixture of magnesia, by adding so much chloride of ammonium to the solution of magnesia that no precipitate was produced by ammonia, upon which the arsenite of ammonia and ammonia were added. After being dried over sulphuric acid, the salt contains no water, and 3 equivs. magnesia to 1 equiv. arsenious acid. The salt was boiled with nitromuriatic acid, and precipitated as ammonio-arseniate of magnesia. Some magnesia remained in solution, which was precipitated by the addition of phosphate of soda. Analysis furnished—

Magnesia	37·9	3 =	60	37·7
Arsenious acid	62·1	1	99	62·3

Arsenite of the Protoxide of Manganese.—The arsenite of ammonia produces, in a solution of the protoxide of manganese, a pale rose-coloured precipitate, which quickly turns brown in air, even during the washing on the filter. If exposed for any length of time to the air, either in the liquid or on the filter, it becomes black. When it is washed, the air being carefully excluded and dried over sulphuric acid, it may be represented by the formula $3MnO, 2AsO^3 + 5HO$. At 212° it loses 1 atom of water. Its decomposition by heat differs from that of the other salts, arsenious acid being volatilized, whilst the residue contains arseniuret of manganese and arseniate of the protoxide of manganese. The salt furnished on analysis—

Protoxide of manganese	29·69	3 =	108	30·73
Arsenious acid	58·50	2	198	56·43
Water.....	11·81	5	45	12·84

In the decomposition of the preceding salt, I have obtained the arsenious acid in a peculiar form, which is perhaps a new modification of the acid. When, for instance, the arsenite of the protoxide of manganese is evaporated with a large excess of muriatic acid, the arsenious acid is precipitated in minute crystalline flakes. The crystals are so minute, that even under the microscope they cannot be distinctly separated from one another, but form snow-white flakes. They dissolve very rapidly in alkalies, acids, and likewise, but in a less degree, in water.—Liebig's *Annalen*, lxxiv. p. 218.

On some new Products obtained by the Action of Sulphite of Ammonia upon Nitronaphthaline. By Prof. R. Piria.

The author has found that the sulphite of ammonia acts powerfully upon organic substances of the type $M^{-n} H^{+n} (NO^4)$, furnishing new products. The nitro-benzoic, carbazotic, nitranisic, and nitro-salicylic acids are so circumstanced. The author has especially studied the action of the sulphite of ammonia upon nitronaphthaline.

When an alcoholic solution of nitronaphthaline, $C^{20} H^7 NO^4$, and a very concentrated solution of sulphite of ammonia are heated together, taking care to keep the liquid neutral during the ebullition, two new acids are obtained combined with ammonia, which the author calls *naphtionic* and *thionaphtamic* acids. The formula for these acids, as they exist in the anhydrous salts, is $C^{20} H^8 NS^2 O^5$. The crystallized naphtionic acid is represented by the formula $C^{20} H^8 NS^2 O^5, HO + Aq$. It is white, almost insoluble in cold water and alcohol, more soluble in boiling water, from which it is deposited on cooling in acicular crystals of a satiny lustre. This acid is sufficiently powerful to displace acetic acid from its compounds; it is very stable, and is scarcely attacked, except by the most powerful oxidizing agents. Thus boiling hydrochloric acid

and sulphuric acid at the temperature 392° do not attack it; boiling nitric acid converts it into a brown resinous matter.

The naphtionates are all soluble, and crystallize easily. The naphtionate of potash is anhydrous; those of soda and of lime contain 8 equivs. water of crystallization.

Thionaphtamic Acid.—This acid cannot be obtained in the free state, but it forms perfectly-defined salts, which have been analysed. The thionaphtamate of potash is represented by the formula $C^{20}H^{8}NS^{2}O^{5}$, KO, the thionaphtamate of baryta by $C^{20}H^{8}NS^{2}O^{5}$, BaO, 3Aq.

The thionaphtamates of potash, soda and ammonia are soluble and crystallize; the others are obtained by double decomposition. On attempting to isolate thionaphtamic acid, it is resolved into sulphuric acid and *naphtalidine* (the naphtalidame of Zinnin, $C^{20}H^{9}N$). By distilling a thionaphtamate, naphtalidine is readily obtained in great abundance.

The author has noticed a property of naphtalidine which had not been previously observed, viz. its conversion, under the influence of perchloride of iron and oxidizing agents, into *naphtameine*, a new substance of a beautiful blue colour, which resembles orcine in some of its properties.

The author concludes, that, under the influence of sulphite of ammonia, the nitronaphtaline is converted into naphtalidine, just as it would be under the influence of the hydrosulphate of ammonia, but with this difference, that the nascent naphtalidine unites with the elements of the sulphuric acid to form two isomeric acid compounds of the formula—

$$C^{20}H^{9}NS^{2}O^{6}=HO+C^{20}H^{8}NS^{2}O^{5}.$$

In this point of view the naphtionic and thionaphtamic acids have the greatest analogy with the acids formed by the action of sulphuric acid upon several organic substances.

The two acids in question present the same case of isomerism as the sulphovinic and isethionic acids, with this difference, that they are formed simultaneously under the same circumstances and in nearly equal quantity. All experiments to convert the one acid into the other have failed.—*Comptes Rendus*, Sept. 30, 1850.

On the Formation of Nitrohippuric Acid in the Animal Œconomy. By Cæsar Bertagnini.

The author has discovered a new fact in examining the modifications which several organic substances experience in passing through the body. Starting from the known fact of the conversion of benzoic into hippuric acid, he found that nitrobenzoic acid introduced into the system gives rise to the production of an acid, which passes into the urine. This acid can be extracted, and presents on analysis the composition $C^{18}H^{8}N^{2}O^{10}$. It must be considered as nitrohippuric acid; and, in fact, the author has prepared from hippuric acid a nitrohippuric acid, identical in its characters with that which

he had extracted from the urine under the circumstances above mentioned. It suffices for this to treat hippuric acid with a mixture of fuming nitric and sulphuric acids.

Nitrohippuric acid, both the artificial as well as that extracted from the urine, is resolved into nitrobenzoic acid and sugar of gelatine when treated with hydrochloric acid.

It is curious to find benzoic and nitrobenzoic acids appropriate the elements of sugar of gelatine in passing through the system, in order to form respectively hippuric and nitrohippuric acids.—*Comptes Rendus*, Sept. 30, 1850.

Action of Chemical Agents on Sulphite of Lead.
By Professor Redwood.

Prof. Redwood has published the result of some experiments he had made, with the view of ascertaining how far sulphite of lead is acted upon and rendered soluble by certain agents which it might be expected to encounter if introduced daily into the stomach with the food. The inquiry had reference to a question which had recently excited some degree of public interest in connexion with a proposed improvement in the manufacture of sugar. A patent had been taken out for this process, which consisted in precipitating impurities from saccharine solutions with subacetate of lead, and subsequently removing any excess of lead by passing sulphurous acid gas through the solution. The lead was thus converted into sulphite, which is so insoluble that it had been found practicable to remove every trace of lead by this means. Many persons conversant with the manufacture of sugar were nevertheless doubtful as to the safety of allowing so deleterious a substance as lead to be used in the preparation of an article of daily food, alleging that from carelessness, or imperfections in the apparatus, or even in the process itself, the public health might be endangered. The results of the investigation instituted by the Government to determine what amount of danger was to be apprehended from the adoption of the patented process had been published in the last number of the Pharmaceutical Journal. The chemists employed by the Government had found lead in minute quantities in the sugar, and in larger quantities in the treacle; and the medical men who had been consulted had expressed opinions to the effect, that danger was to be apprehended from the daily consumption of an article of food containing these quantities of lead. Opinions had however been expressed on the other side of the question. Dr. Gregory had made some inconclusive experiments by administering sulphite of lead to animals, and had come to the conclusion, in which Mr. Brande concurred, that it was *perfectly innocuous, and as harmless as so much chalk*. "This," he says, "might be predicted from its excessive insolubility and very stable nature, arising from the powerful affinity of sulphurous acid for oxide of lead; this prevents the formation of carbonate (white lead), which is truly the poisonous lead compound." It was this statement, and others to the same purport,

which had suggested the experiments about to be described. Sulphite of lead had been represented as innocuous in consequence of its great insolubility and very stable nature; it appeared desirable therefore to determine, not only whether it be stable and insoluble when treated with distilled water, which is of very little consequence with reference to the question practically at issue; but whether it be equally unaffected when submitted to the chemical agents to which it would be subjected when introduced into the stomach.

1. *Action of Water and Acetic Acid on Sulphite of Lead.*—Sulphite of lead was prepared by passing sulphurous acid gas through solution of acetate of lead. The whole of the lead was found to be thus precipitated, and none could be detected in the liquor, even after standing in contact with the precipitate for several days.

2. *Action of Hydrochloric Acid on Sulphite of Lead.*—Water acidulated with hydrochloric acid speedily decomposes sulphite of lead; and the liquor, after standing for some time, affords a white precipitate of carbonate of lead on the addition of carbonate of soda, and an abundant black precipitate with sulphuret of ammonium.

3. *Action of Chloride of Ammonium and Chloride of Sodium on Sulphite of Lead.*—On macerating sulphite of lead in solution of chloride of ammonium, the liquor was found to be largely impregnated with lead, affording precipitates with carbonate of soda and with sulphuret of ammonium. The action of chloride of sodium on the sulphite was much less marked than that of the preceding salt, the tests affording only a slight indication of the presence of lead in the liquor.

4. *Action of Lactic Acid on Sulphite of Lead.*—The liquor resulting from the maceration of sulphite of lead in a weak solution of lactic acid afforded evidence of the presence of lead in small quantity, the amount being rather greater than that taken into solution by the action of chloride of sodium.

5. The sulphite of lead being acted upon so quickly, and the lead rendered soluble by hydrochloric acid, it was concluded that free hydrochloric acid, added to a weak solution of a soluble salt of lead, would prevent the precipitation of the lead by sulphurous acid; and this was found to be the case. A solution, prepared as above, in which sulphurous acid gave no precipitate, afforded precipitates with carbonate of soda and with sulphuret of ammonium.

6. *Action of Carbonate of Soda on Sulphite of Lead.*—With the view of determining whether the affinity between sulphurous acid and oxide of lead be so powerful as to prevent the formation of carbonate of lead, as stated by Dr. Gregory, 10 grs. of sulphite of lead were added to a solution of 20 grs. of carbonate of soda in 4 oz. of distilled water. After standing for two or three days, without the application of heat, the insoluble salt was collected on a filter, and treated with dilute acetic acid. The liquor thus obtained gave copious precipitates with carbonate of soda and with sulphuret of ammonium, thus proving that the sulphite had been partly converted into carbonate by the action of a weak cold solution of carbonate of soda.—*Pharmaceutical Journal*, November 1850.

On the Extraction of Iodine from Plants and from Coal. By M. Bussy.

Some doubts having been expressed by several persons in the Academy with respect to the accuracy of the statements respecting the existence of iodine in certain plants, the author deposited a specimen of cress and of the iodine which he had obtained from it, and also of iodide of potassium procured from the same plant.

M. Bussy also remarks that in 1839 he showed that the coal of Commentry contains iodine. Some portions of this coal contain much sulphuret of iron; whence it happens that whilst working, masses often undergo a kind of slow combustion. The heat thus produced gives rise to thick vapours which condense on the surface, and the product is found to consist of sulphuret and other arsenical compounds, with much sal-ammoniac, containing hydriodate of ammonia; at the period mentioned the author merely stated the peculiar reactions of iodine, without trying to isolate it. Not having any of the natural product in his possession in which he had first met with iodine, he had recourse to the products of the distillation of coal for obtaining gas; and he found in the ammoniacal liquor a considerable quantity of iodine, and such as he could separate and estimate.

The process which he adopted was to add to a certain quantity of the condensed water enough potash to convert the hydriodate of ammonia into iodide of potassium; by evaporation to dryness and calcination, the tarry matter was destroyed: and the residue, being treated with alcohol, yielded iodide of potassium. The iodine was estimated in the form of iodide of palladium, by the decomposition of which by heat iodine was obtained, of which a specimen was presented to the Academy.

Three kilogrammes of the condensed water of the establishment at the barrière of Fontainebleau yielded 0·59 gr. of iodine, nearly 0·2 per kilogramme, or 2 ten-thousandths: iodine was also found in the liquor of another establishment, which renders it probable that it will be found in all varieties of coal.

M. Bussy remarks that the quantity stated does not include the whole of the iodine contained in the coal, since a quantity remains in the coke, which may be obtained by incineration.

M. Bussy observes, that the distilled product of gas-works may possibly be employed for the œconomical preparation of iodine, especially if it could be obtained without prejudice to the separation of the ammoniacal salts.—*L'Institut*, No. 853.

On the Existence of Bromine in the Products of the Distillation of Coal. By M. Mène.

The author, who is chemical assistant at the College of France, states that he has discovered bromine in the ammoniacal liquor obtained as above mentioned. He has also found the iodine previously mentioned by M. Bussy.—*Ibid.* No. 854 and *Phil. Mag.*

ANALYTICAL CHEMISTRY.

On the Detection of Lithia in the Presence of Soda by the Blowpipe. By E. J. Chapman, *Professor of Mineralogy in Univ. Coll., London**.

The red colour imparted by lithia compounds to the blowpipe flame is well known to be entirely destroyed by the presence of soda. Stein has stated†, that the characteristic crimson colour may be rendered visible, even when a large proportion of soda is present, by fusing the mixture on a platinum wire, saturating it with tallow, and again igniting it by the unaided flame of a candle, excess of temperature being, in his opinion, the principal cause by which the soda flame prevails to the obliteration of that produced by lithia. This method is however by no means infallible; the reaction, if obtained at all, can last but for an instant; and as the tallow in its combustion frequently produces a reddish-yellow flame, and always an intense blue one sufficient in itself to prevent the momentary reaction from being properly seen, conviction of either the presence or absence of lithia will rarely be established in the operator's mind. Some other less uncertain method is therefore desirable; and the following will, I think, be found to answer the purpose:—

The assay, which we will here suppose to consist of the two substances in question, is to be fused in a good blast with chloride of barium on a loop of platinum wire. Decomposition readily takes place; alkaline chlorides are formed and volatilized; but, contrary to what is generally stated in chemical works respecting the volatilization of these compounds, the chloride of sodium is driven off before the chloride of lithium, so that the powerful yellow flame at first produced gradually diminishes; and by-and-by a thin green light, occasioned by baryta, is seen to stream from the point of the wire as the assay shrinks down into the coil of the loop. If this latter be then advanced within the edge of the blue flame, the red coloration will quickly ensue, and endure sufficiently long to prevent the slightest chance of misconception or uncertainty.

To satisfy myself thoroughly in this respect, I prepared a mixture of 2 parts of ignited carbonate of soda with 1 part of carbonate of lithia, and placed portions of this in six little porcelain capsules, distinguished upon their under sides by a spot of ink. Then into six similar capsules, but without the ink spots, I placed portions of carbonate of soda only, and arranged the twelve indiscriminately upon a tray, in such a manner that I could not recognise one from another. On testing each of these by the above method, I found to my satisfaction that I could correctly separate, and without hesitation, the six containing lithia from the others. The only point to be attended to in order to ensure success, or rather to avoid the least chance of failure, is to have a clear, sharp, and not too large a flame, especially when the lithia reaction begins to manifest itself.

* Communicated by the Author.

† Journ. für Prakt. Chem., xxxi. 362.

On the Copper Test for Sugar. By M. LASSAIGNE.

It has been long known, according to the experiments of M. Frommherz, that tartrate of copper dissolved in a solution of potash is easily reduced when heated with glucose, and converted into sub-oxide of copper. The same author has stated that cane-sugar, which differs in composition from glucose, does not act upon this reagent. It is on these facts that M. Barreswil has founded his process for estimating the quantity of sugar.

The employment of this reagent is even indicated, in several recent chemical works, as capable of distinguishing between cane-sugar and glucose.

The alkaline solution of copper, employed as a test liquor, is prepared by two published methods; one by M. Barreswil, and the other by M. Poggiale. The first consists in dissolving with heat, in one-third of a litre of distilled water, 50 grammes of bitartrate of potash, and 40 grammes of carbonate of soda, and afterwards adding 30 grammes of powdered crystallized sulphate of copper; after boiling, allow the solution to cool, and lastly add 40 grammes of potash dissolved in one-fourth of a litre of water; it is made up a litre and again boiled. The second method, proposed by M. Poggiale to determine the presence of sugar of milk, which also reduces the oxide of copper, like glucose, consists in dissolving in 200 grammes of water 10 grammes of crystalline sulphate of copper, 10 grammes of bitartrate of potash, and 30 grammes of potash. This solution when filtered is of an intense blue colour, and ought to be kept in the dark.

The trials made with this solution proved that cane-sugar or beet-sugar may produce the same reaction as glucose on the alkaline solution of oxide of copper, according to the conditions of operating and the modifications which this kind of sugar may undergo by the influence of heat alone, or with water.

M. Lassaigne thinks he has ascertained that glucose acts more readily, and at a lower temperature, on the copper reagent than common sugar does; but the latter, if heated till it begins to assume an amber colour of less or greater depth, then acts like the former. In fact, an aqueous solution of glucose artificially prepared with starch, and containing one-fiftieth of its weight of this sugar, treated with the copper test at a heat of 64° to 68° F., reacts in less than three or four minutes, or by holding the tube inclosed in the palm of the hand. Under similar conditions cane-sugar produces no effect on the solution of copper; but it may be kept for some time near 212° without giving any appearance of reduction. By prolonging the time of boiling, action is at first perceived by change in the blue colour of the solution, slight turbidness, and the separation of a pulverulent yellow precipitate, which eventually becomes brick-red.

The action of cane-sugar, not modified by heat, is slow upon the alkaline solution of copper; whereas when it has been subjected to a more or less high temperature, the action is often as prompt as that of glucose on the same reagent.

Heat, by its action on cane-sugar, ought naturally to put us on

our guard in employing the solution of copper above mentioned for determining glucose in manufactured products in which it is supposed to exist. The employment of this reagent is to be suspected of inducing error in certain cases; thus barley-sugar and *pâte de gomme*, prepared with cane-sugar slightly *caramelized* by heating the substances which enter into their composition, acted as readily on the test as pure glucose.

It has also been proved that potash, which acts in so characteristic a manner upon glucose, and which has been proposed for distinguishing this kind of sugar from cane or beet-sugar, often gives with these latter sugars reactions analogous to those developed by glucose. In the examination of sugars, and various alimentary or medicinal preparations into which they enter, the influence which heat may produce on these products, and the modifications which result from it, should be considered.—*Journ. de Chim. Méd.*, Juillet 1850.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new Process for ascertaining the Value of Indigo. *By* Dr. Bolley.

Of the numerous methods of testing indigo, those based upon the destructive action of chlorine upon the colouring principle of the indigo have found most favour in the eyes of the manufacturer. The experiments to reduce the indigo-blue and to separate it are tedious, and by no means deserving great preference as regards accuracy of the result. The same may be said of Chevreul's method of dyeing cotton until the indigo solution is exhausted. The proposition of determining the value of indigo from the degree of its solubility in sulphuric acid must be entirely rejected, for reasons which every chemist will be well acquainted with; and lastly, the measuring the intensity of the colour of a solution diluted to a certain degree is of very little value, as it is quite impossible, with different kinds of indigo, to prepare solutions possessing the same power of transmitting light, the sulphatic solutions of some kinds having a strong reddish tint, others not; and further, because some constituents may easily remain undissolved in the sulphuric acid, either from being insoluble or from imperfect contact with the acid; because moreover an approximative comparison of the depths of the colour is only possible with very considerable dilution; and lastly, because of the inconvenience of having to keep a normal liquid (which is constantly changing), or of having to make a fresh one for every experiment.

The methods which are founded upon the use of chlorine are likewise not free from objections. Their evils are owing partly to the properties of the indigo, but also in part to the chlorine solutions employed.

For instance, when pure indigo-blue is compared with commercial

indigo, assuming the amount of colouring principle to be proportional to the quantity of chlorine consumed, the result always proves too much in favour of the indigo, because, besides the blue pigment, upon which alone the value depends, other organic substances are contained in the indigo which also remove chlorine from the test-liquor. Berzelius correctly judges this source of error to be very small when treating of the methods of determining the value of pigments in his manual. Schubart goes still further; he says it is well known that chlorine acts only on the indigo-blue, not upon the indigo-brown and indigo-red, and very slightly upon the indigo-gluten. Schlumberger also states, that he has convinced himself that chlorine has no action upon the constituents of the indigo mixed with the blue pigment. It cannot however be admitted that chlorine has no destructive action upon these substances, but it is true that it is far less violent than upon the indigo-blue. The error is not of sufficient importance to make it necessary to reject the entire principle; and it becomes still less when the different kinds of indigo are compared with each other, and not with pure indigo-blue.

The other error is of far more consequence. I consider it insuperable. Chevreul, Schlumberger and others have recommended chlorine-water and a solution of chloride of lime for the colorimetric liquid. But who does not know how difficult it is to find two chlorides of lime of exactly the same strength, or to preserve a solution of chloride of lime or of chlorine-water without their being decomposed? When it is advised to determine the strength of the solution of chloride of lime by diluting it until it is capable of decolorizing a fixed measure of a normal solution of indigo, this evil is added, that we are either restricted to a variable solution of indigo, or have always to prepare a fresh solution each time that it is requisite to prepare the chlorine solution. But this is far too tedious.

A constant source of chlorine will enable us to avoid all these inconveniences; and this we possess in the use of hydrochloric acid and chlorate of potash. The simplest theoretical consideration will show that the quantities of chlorine disengaged must be in exact proportion to the quantities of chlorate of potash employed. For our present purpose it is quite immaterial whether the liberated gas is chlorine or hypochlorous acid with chlorine, the euchlorine discovered by Davy, if only the relative proportion of the constituents remain constantly the same, and consequently possess the same decolorizing effect for like quantities of the substances consumed to produce that effect. If therefore during the process we take care that there is no deficiency of muriatic acid, then we may be sure that the object has been perfectly attained, viz. that of being able to estimate correctly the amount of chlorine disengaged from that of the consumed chlorate of potash.

I proceed in the following manner:—1 grm. of indigo is rubbed to a fine powder in a porcelain mortar, about 10 grms. of fuming sulphuric acid poured over it, and then left covered from six to eight hours, being now and then stirred. After this time the whole is poured into a strong evaporating dish containing 2 lbs. of water,

50 grms. of strong muriatic acid added, and the whole heated to boiling over a spirit-lamp. The water which escapes during the evaporation is now and then replaced, as far less hydrochloric acid is lost from a dilute solution. A solution of the chlorate of potash is now made as follows:—$\frac{1}{4}$ of a grm. of the warm powdered dry salt is dissolved in 100 grms. of water in a graduated cylinder capable of containing 100 cub. centim. of water. This quantity of salt suffices even for the very best kinds of indigo which I have tested. At first several cubic centimetres of the solution may be added at once, but subsequently only one degree at a time, and the mixture boiled between every addition. The liquid passes from blue into green, brownish-green, and lastly into brownish-red. Any one who has once made the experiment will not fail to hit the right moment when to stop; it is when the liquid has lost the last tint of greenish-brown, and turns reddish-brown. It is well to make a mark with a glass rod moistened in the gradually changing solution upon a strip of white filtering paper. A large series of similar experiments have been made by me and under my direction, and the degrees of chlorate of potash consumed by the different experimenters always coincided to within 1 and $1\frac{1}{2}$ per cent.:—

		Cub. centims. of solution of chlorate of potash consumed.
I. Java	I.	51
	II.	52
II. Bengal	I.	56
	II.	56
III. Java, very inferior	I.	12
	II.	12
IV. Egyptian, very good	I.	40
	II.	41·5
V. Java, inferior	I.	30·5
	II.	31·5
VI. Bengal, good red-violet FF	I.	48
	II.	47

The values might, by calculation or a different arrangement of the apparatus, be reduced to those of pure indigo-blue; but that appears useless, as indigo-blue is not an article of commerce, and the consumer or purchaser is satisfied when he has ascertained the value of the samples compared with kinds known by him to be good. Moreover there would be this danger, that one person testing might obtain other results with his indigo-blue (considered by him to be pure) than another; and although this could only arise from the different degree of purity of the indigo-blue, it might lead to the method being considered not trustworthy.—Liebig's *Annalen*, 1850.

On Malleable Brass. *By* Dr. L. Elsner.

It is known that common brass, containing from 27·4 to 31·8 per cent. of zinc, and from 71·9 to 65·8 per cent. of copper, is not malleable while hot, but that articles of it must be made by casting. As it would be of great importance in many branches of industry to

have an alloy of this kind that could be worked while hot, like malleable iron, the information that such an alloy exists must be welcome to artists. As far as I know, the first specimens of malleable brass came from England to Hanover, and the first account of the analysis of this alloy was published by the 'Gewerb-Verein' of Lower Austria at Vienna. The results gave a composition of 34·76 zinc and 65·03 copper, with traces of lead.

On the basis of this analysis, M. Machts, proprietor of a manufactory, made larger specimens of the alloy in question, and found that, by melting together 33 parts of copper and 25 parts of zinc, there was a loss of 3 parts; thus making 60 per cent. copper and 40 per cent. zinc. It differs from the English specimens by containing a larger proportion of zinc, and possesses, according to M. Machts, the precious property of malleability in a higher degree than the English specimens.

A piece of "*yellow metal*," similar in colour to this alloy, was found on analysis to contain 60·16 copper and 39·71 zinc, which is the composition of malleable brass. It also showed great density, or solidity.

I caused an alloy to be made by melting together 60 parts copper and 40 parts zinc, which had the following properties:—The colour was between that of brass and tombac, it had a strong metallic lustre, a fine close-grained fracture, and great solidity (density). Its specific gravity, at the temperature of 50° F., was 8·44; by calculation it should only have been 8·08, thus showing that in the formation of the alloy a condensation must have taken place. Calculation shows that the alloy may be considered as a determinate chemical combination, for the results of the analysis very nearly accord with the assumption that it may be considered as composed of 3 atoms by weight of copper and 2 atoms by weight of zinc ($3Cu+2Zn$). The hardness of the alloy is the same as that of fluor spar; it can be scratched by apatite, consequently its hardness is $=4$. The alloy is harder than copper, very tough, and is, in a properly managed fire, malleable; so much so that a key was forged out of a cast rod.

These important properties of this alloy warrant an expectation of its application to many purposes in the arts, and it would appear that they depend on its definite chemical proportions. Agreeably to the directions of M. Feyerabend, care must be taken, in melting together the metals, not to permit too great a loss of zinc to take place, lest the proportion between the metals should be altered, which might not be without effect on the important properties of the alloy. With this view, it might be advantageous in practice, in place of zinc, to add, in melting, a proportionate mixture of brass to the proper proportions of copper. An alloy prepared in this way gave on analysis 61·44 copper and 38·15 zinc. It is very probable that malleable brass will hereafter, in many cases, be made use of instead of the higher-priced copper.—*Verhandlungen des Vereins zur Beförderung des Gewerbfleisses in Preussen*, 1849; *and* Newton's *Journal*.

PATENTS.

Patent granted to Thomas Irving Hill *for Improvements in the Treatment of Copper and other Ores.*

This invention consists, first, in certain improvements in treating copper ores, to obtain products therefrom; and, secondly, in improvements in the treatment of iron ores.

The first part of the improvements in treating copper ores relates more particularly to what are called refractory ores. In smelting copper ores, fluxes are used to facilitate the process; and this part of the invention consists in the employment of a flux composed of galena, or sulphuret of lead, combined with baryta, carbonate or sulphate of baryta, or carbonate or sulphate of strontia, the combination of galena and baryta being preferred; the galena increases the general fusibility of the mass, and improves the quality of the copper. The patentee states, that he is aware that it has been before proposed to use the sulphate of baryta combined with other matters as a flux, and he does not therefore claim the same when separately used. The ingredients are to be mixed in the proportion of one-tenth of galena to seven-tenths of baryta; and this flux is to be introduced into the furnace in the ordinary manner. The workman will use such quantities of the flux as the nature of the ore requires; but the patentee states, as a guide, that when treating ores of an average of 12 per cent. of copper, the flux should be employed in the proportion of about one-eighth of it to seven-eighths of the ore. The flux may be introduced into the ore when in the melting and roasting furnaces.

Another improvement consists in a mode of applying prepared oxygen gas to the calcining, roasting and melting furnaces, so as to promote the acidification of the volatile matters and the oxidation of the iron and other extraneous metals that may be contained in the copper ores; and also in employing such gas to facilitate the combustion of the smoke arising from the burning of the coal in the furnace. The patentee says, that he does not claim the use of oxygen gas generally in the treatment of copper ores, as the same has been before used. He obtains the oxygen gas by introducing black oxide of manganese into retorts, situated near the calcining furnaces, and submitting the same to a high degree of heat; and he conducts the gas from the retorts, through tubes, into a receiver or gasometer (supplied with water, like those used in the manufacture of coal-gas), and thence, through other tubes, into the furnaces, which it enters through openings in the sides of the furnace or over the bridge, and, mixing with the products of combustion, ignites the same.

The improvements in treating iron ores consist, first, in the use of carbonate of baryta as a flux, which is to be mixed with the iron ore before it is introduced into the furnace; and, secondly, in the employment of oxygen gas, obtained in the manner above described, to facilitate the process of smelting the ore, the gas being used in the same way as when treating copper ore.—Sealed March 9, 1850.

Patent granted to J. E. Disbrowe Rodgers *for Improvements in the Manufacture of White Lead.*

This invention consists in manufacturing carbonate of lead, commonly called white lead, by subjecting metallic lead to the united action of a certain temperature, atmospheric air, aqueous and acetic acid or pyroligneous acid vapours and carbonic acid gas, in such manner as to have the process completely under the control of the operator.

The improved process of manufacturing the carbonate of lead is carried on in a chamber which is capable of being heated by steam-pipes or other means, and is so constructed as to admit of it being made dark and air-tight, or nearly so, and to permit the escape of vapours and gases when required. This chamber is fitted with wooden frames, from the ceiling to the floor, provided with cross pieces of the same material for supporting the lead, and so arranged that the operator may pass between the rows, in order to watch and regulate the conversion of the same into carbonate of lead. Troughs or vessels are placed upon or let into the floor of the chamber, some of them being designed to contain a fluid undergoing vinous fermentation, and thus to supply carbonic acid gas; and the others (into which pipes from a steam-boiler, furnished with stop-cocks, dip), being intended to contain weak vinegar, dilute pyroligneous acid, acid wine, sour beer, or a liquid undergoing acetous fermentation, for the purpose of supplying acetic acid vapours by the means hereafter mentioned.

The lead to be operated upon is cast in sheets, 3 or 4 feet long, and about one-eighth of an inch thick; and these sheets are doubled and hung upon the wooden frames as close together as possible without touching. The first-mentioned troughs or vessels are now charged with an infusion of malt with sugar (formed by adding 8 gallons of boiling water to 1 peck of malt and 2 lbs. of sugar), or any other liquid capable of undergoing the vinous fermentation spontaneously or when mixed with yeast or other fermenting agent. The other troughs or vessels are supplied with weak vinegar, dilute pyroligneous acid, acid wine, sour beer, or a liquid undergoing acetous fermentation; and the temperature of the chamber is raised, by the steam-pipes or other means, until it is between 70° and 80° F. When the vinous fermentation is fully established, and carbonic acid gas is being evolved in the chamber, it is darkened and closed as perfectly as possible; and then steam is admitted from the boiler, through the pipes, into the weak vinegar or acid liquor, so as to charge the chamber with aqueous and acetic acid vapours. The introduction of steam into the chamber must be continued for an hour, and be repeated three or four times in every twenty-four hours; and the temperature of the chamber must be maintained between 70° and 80°, which may be ascertained by placing a thermometer with its bulb in the chamber and its stem outside the same. The operator must enter the chamber, in order to renew the fermenting and acid liquids once in every forty-eight hours during the progress of conversion, which is usually complete in about twelve days.—Sealed August 1, 1849.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Styracine. By Dr. J. WOLFF.

THE styracine from liquid storax, which has recently been the subject of some very interesting investigations, was isolated by E. Simon, and decomposed by him into cinnamic acid and a volatile substance, which he called styracone, and which was subsequently analysed by the late Professor Marchand. Toel*, who examined the same subject, obtained results which differed somewhat from those of Marchand. He regarded styracine as a compound analogous to the natural fats, and found that the volatile substance produced by the action of solution of caustic potash upon styracine, and which he called styrone, was crystallizable. Upon this Strecker† drew attention to the circumstance, that styrone, for which he advanced a different formula, stood in the same relation to cinnamic acid as vinous alcohol to acetic acid, and that it was consequently the alcohol of cinnamic acid. I have made some experiments on this point, and have succeeded in confirming the view that styrone is a new alcohol.

For preparing the styracine, Toel's method was followed with some modifications. Liquid storax furnishes, on distillation with carbonate of soda, styrole, and the residue consists of styracine mixed with cinnamate of soda and resin. The crude styracine, after being washed, is mixed with cold alcohol, when in the course of two or three days, frequently by the next morning, it has become crystalline throughout, can be dissolved in alcohol, mixed with acetate of lead, and so be easily separated from the resin. By repeated crystallization from alcohol and æther, and at last from pure æther, or by pressure between bibulous paper, it is obtained of a dazzling white colour and perfectly pure. It is difficult to purify styracine by means of animal charcoal. So long as it is not quite pure, it turns brown in the air. On dissolving styracine in alcohol and æther, long before crystallization commences two layers are formed; the upper one is clear and transparent, and contains chiefly the æther, with a little but perfectly pure styracine in solution; the lower one is the alcoholic solution; it is usually somewhat yellow, contains nearly the whole of the styracine, becomes turbid after a

* Chem. Gaz., vol. vii. p. 249. † Ibid., vol. vii. p. 273.

time, and solidifies to a tissue of crystals on contact with a sharp body. Styracine, obtained in the above manner and dried in the air, was burned with oxide of copper and perchlorate of potash, when it afforded—

	Toel.			Strecker.		Wolff.	Calculated.
Carbon	82·57	82·61	82·15	81·47	81·37	82·57	81·90
Hydrogen ..	6·49	6·36	6·16	6·09	6·06	6·37	6·04
Oxygen	10·94	11·03	11·69	12·44	12·67	11·06	12·06

For the preparation of styrone, styracine is submitted to distillation in a spacious retort with a solution of potash of 1·20 spec. grav. When a more dilute solution is employed, only water passes over at first until the proper degree of concentration is attained. A copious separation of cinnamate of potash renders it necessary, when much styracine has been taken in comparison to the solution of potash, to free the retort from time to time of this substance by washing with hot water, and to submit the insoluble styracine again to distillation with fresh solution of potash. I also think that I have observed that a concentrated solution of potash converts the styrone at the moment of its production into cinnamic acid, as with a more dilute potash and the continual addition of water the amount of styrone is by far greater and that of the cinnamic acid less, so that the distillation may be carried on for days without changing the retorts. When pure styracine is employed, the solution of potash remains perfectly colourless.

To avoid the distillation with concentrated solution of potash, and the losses which so readily occur by the breaking of the retorts, styracine may be boiled with an alcoholic solution of potash until it has dissolved in it. On cooling, a large quantity of cinnamate of potash crystallizes out; the solution is then mixed with water, when styrone and any styracine present are deposited, which are separated by distillation.

The milky distillate becomes clear after standing for some time, and the styrone separates at the bottom of the vessel in minute oily drops, which were sometimes obtained minutely divided like a fine meal. I preferred agitating the whole of the distillate with æther, and separating the æther dissolved in the water by chloride of sodium; by allowing it to evaporate in a warm spot, it is separated from æther, and by distillation over chloride of calcium from water; after some time the whole liquid solidifies to a hard crystalline mass, which melts already by the warmth of the hand, and whose boiling-point was found to be 482° F. Styrone consists consequently, like styracine, of two modifications, which do not differ by containing more or less water. The vapour of styrone attacks caoutchouc tubes, and dissolves them quickly; that which passes over last is always coloured yellow, on which account the receiver must be changed several times. The liquid modification of styrone does not become solid at 14° F. It furnished, on combustion with oxide of copper and perchlorate of potash—

	Toel.		Wolff.		Calculated.
Carbon	80·2	80·6	80·1	80·8	18 = 80·62
Hydrogen ..	7·7	7·6	7·3	7·7	10 7·45
Oxygen	12·2	11·8	12·6	11·5	2 11·93

The most decided proof that styrone is the alcohol of cinnamic acid consists in its ready conversion into cinnamic acid.

Hydrate of potash was first used to convert the styrone into cinnamic acid. When styrone is boiled with a solution of caustic potash, to which some solid hydrate of potash is added, it turns first yellow, then red, and later, when the residue has almost become hydrate of potash, dark brown; but it always remains liquid, and does not mix with the ley. At the same time a large amount of styrone passes over undecomposed, and there is scarcely a perceptible evolution of gas, or none. The residue in the retort dissolves entirely in water, and gives a white precipitate with acids, which dissolves readily in alcohol and in æther, and is left on evaporation as a tenacious oily mass, which could not be obtained crystallized. Probably the hydrate of potash has a further decomposing action upon the cinnamic acid, so that it is difficult to stop the operation at the right moment.

When styrone is added to a mixture of peroxide of lead and a concentrated solution of caustic potash, and heat applied, the mass solidifies; at a higher temperature it melts, the peroxide is reduced to oxide, or even to metallic lead, and the distillate contains a quantity of oil of bitter almonds, easily recognized by its physical properties. The alkaline residue contains a large amount of cinnamic acid; it is exhausted with boiling water, separated by filtration from the lead, and mixed with acetic acid; the acid is at once obtained crystallized, when the alkaline solution is heated to boiling, then neutralized with acetic acid, and set aside to cool. It was recrystallized from alcohol and burnt with oxide of copper. It furnished—

Carbon	72·88	73·08	18 = 108	72·97
Hydrogen	5·69	5·81	8	5·41
Oxygen	21·43	21·11	4	32 21·62

To determine the atomic weight, a silver salt was prepared by dissolving the acid in ammonia, and precipitating with nitrate of silver. It was dried at 212°, and furnished 41·9–42·3 per cent. of silver. Theory requires 42·3.

The oil of bitter almonds must be considered as a further product of decomposition of the cinnamic acid, of which a portion is again destroyed by the action of the oxygen, while another is still being formed.

When styrone is heated in a retort with a large quantity of nitric acid, in which it does not dissolve and by which it is scarcely acted upon, a considerable amount of oil of bitter almonds is also obtained in the distillate, much nitrous acid is given off, and the residue solidifies entirely or upon the addition of water. It was separated by washing from the nitric acid, recrystallized from alcohol, and

then the silver salt prepared and analysed; it furnished 42·9–42·6 per cent. of silver. These numbers correspond to the composition of the benzoate of silver, which contains, according to the formula $C^{14} H^5 O^3 + AgO$, 42·8 per cent.

We consequently obtain in this manner only the further products of decomposition of cinnamic acid, which decomposition must be ascribed to the nitrous acid, as pure nitric acid converts cinnamic only into nitrocinnamic acid. On this account, in a second experiment, the production of the nitrous acid vapours was prevented by the addition of urea, which, as is well known, is thus decomposed into nitrogen and carbonic acid. The quantity of oil of bitter almonds obtained in this experiment was much smaller, and the residue furnished an acid which formed light yellow groups of crystals on being recrystallized from alcohol, and proved, by its insolubility in water and sparing solubility in alcohol, to be nitrocinnamic acid. The analysis of the acid, dried at 212°, gave—

Carbon	55·6	18 =	108	55·9
Hydrogen	4·0	7	7	3·6
Nitrogen	..	1	14	7·3
Oxygen	..	8	64	33·2

By oxidation with chromate of potash and sulphuric acid, or still better with chromic acid, of which large quantities are required, cinnamic acid is likewise obtained, but it is coloured green by oxide of chrome. The mixture evolves considerable heat; boiling must be avoided, as the cinnamic acid is further decomposed, which is rendered evident by the disengagement of oil of bitter almonds. On cooling, the cinnamic acid separates on the surface; it was once obtained in beautiful plates and perfectly pure; but in general it is amorphous and contaminated with oxide of chrome, which even follows it into the alcoholic solution; it can be separated by adding some water to this, when the oxide of chromium is precipitated with a little cinnamic acid; it is filtered, and the remainder of the cinnamic acid thrown down by water.

It results from this investigation, that styrone is really converted, by the assimilation of 4 equivs. oxygen, into cinnamic acid—

$$\underset{\text{Styrone.}}{C^{18} H^{10} O^2} + O^4 = \underset{\text{Cinnamic acid.}}{C^{18} H^8 O^4} + 2HO,$$

and that in this respect styrone may be reckoned among the alcohols. I regret that want of time prevented me from ascertaining some of the relations between styrone and the alcohols we are acquainted with.

According to a qualitative experiment, styrone forms a conjugate compound with sulphuric acid. When fuming sulphuric acid is poured over it, it acquires a dark purple colour, congeals to a viscous mass, and forms, when neutralized with carbonate of baryta, a soluble salt of baryta.—Liebig's *Annalen*, September, 1850.

On Anhydrous and Crystallized Iodic Acid.
By V. A. Jacquelain.

The author examines practically and theoretically the value of the different known processes for the preparation of iodic acid. The following are the conclusions arrived at:—

1. The action of chlorine upon iodine, and that of the chlorate of potash, require too careful manipulations to be employed on a large scale.

2. That of dry hypochloric acid gas and iodine is too tedious and expensive.

3. The use of nitric acid of 1·5 spec. grav. and iodine furnishes quickly, cheaply, and without much manipulation, a large amount of very pure, crystallized, anhydrous iodic acid, with which all the hydrates of M. Millon may be prepared.

4. The action ascribed to small quantities of nitric acid upon the chlorate of potash is improbable, as far as relates to the production of iodic acid.

5. In the reaction of sulphurous acid upon a solution of iodate of baryta, no sulphate of baryta is formed.

6. In the presence of certain proportions of acid, iodate of baryta and sulphuric acid, the latter may not exhibit the characteristic reaction with baryta.

7. Iodic acid colours the protosulphate of iron in pure concentrated sulphuric acid in the same manner as nitric acid and the nitrates.

8. The equivalent of iodine is 1570, instead of the old numbers 1579 and 1586.—*Comptes Rendus*, October 28, 1850.

On the Sulphuric and Nitric Compounds of Benzine and Naphthaline. *By* A. Laurent.

The recent paper of M. Piria* on sulphonaphtalidamic acid, has induced me to publish my investigations on the same subject. I had considered nitrobenzide, aniline, nitronaphtaline and naphtalidam, as derivatives by substitution of benzine and naphthaline, and as having consequently more or less analogy with the latter. It is well known, that, by treating several of them with sulphuric acid, the sulphobenzidic, sulphanilic, sulphonaphtalic and nitrated sulphonaphtalic acids are obtained.

These same acids may be obtained by other processes; thus, on treating sulphonaphtalic acid with nitric acid, nitrated sulphonaphtalic acid, SO^3, $C^{10}H^7X$, is formed; when this latter is placed in contact with sulphuret of ammonium, sulphonaphtalidamic acid, SO^3, $C^{10}H^7Ad$, is obtained. This may also be procured from the naphtalidamic carbamide by heating this with concentrated sulphuric acid; carbonic acid is instantly disengaged, and the liquid, on being diluted with water, deposits sulphonaphtalidamic acid. We have—

$$2SO^4H^2 + C^{21}H^{16}N^2O = 2SO^3C^{10}H^9N + CO^3H^2.$$

Carbamide.

* See page 436.

By continuing the action of nitric acid upon sulphonaphtalic acid, binitrated sulphonaphtalic acid is formed, the ammonia salt of which, crystallizing in beautiful yellow needles, contains $SO^3\ C^{10}\ H^6\ X^2 + H^3\ N$. This salt, on treatment with sulphuretted hydrogen, deposits some sulphur, and a new nitrated acid is formed, which appears to be the nitrated sulphonaphtalidamic acid, $SO^3 C^{10} H^6 X Ad$.

Although nitrated naphtalidam is not known, I believe that this base is formed on treating binitrated naphthaline with sulphuretted hydrogen, as on performing this operation I obtained a carmine-red alkali, which melted in a closed vessel under the influence of heat.

It is known, that, on treating benzine successively with nitric acid, sulphuretted hydrogen and sulphuric acid, sulphanilic acid is formed. It may also be obtained in the following manner :—Sulphobenzidic acid is boiled with nitric acid, when a new acid, the ammoniacal salt of which contains $SO\ C^6\ H^5\ X + H^3\ N$, is formed. This consequently is the nitrated benzidate of ammonia. By treating this with sulphuretted hydrogen, sulphanilate of ammonia is produced.

On pouring a little nitric acid into nitrated phtalate of ammonia, an acid salt is deposited, which contains $C^8\ H^5\ XO^4 + H^3N + 2Aq$. By heating this salt until it begins to fuse, it loses water, and is converted into nitrated phtalimide, which contains $C^8 H^4 X NO^2$.—*Comptes Rendus*, October 14, 1850.

On Ætherification and a new Class of Æthers. *By* G. Chancel.

The recent publication of a paper by Prof. Williamson on ætherification* compels me to bring before the Academy the results, although still imperfect, of the researches which I have undertaken on the same subject, but which the want of the necessary materials has prevented me from completing. Without wishing in any way to make a claim of priority, I merely desire to state, that Mr. Williamson and myself have arrived at the same time, and independently, at identical results, although by a slightly different method.

These results entirely confirm the ideas enounced by M. Gerhardt respecting the equivalent of alcohol and æther, and according to which these two bodies should be represented by formulæ containing the same amount of oxygen, either by $C^4\ H^{12}\ O^2$ † and $C^8\ H^{20}\ O^2$, or by $C^2\ H^6\ O$ and $C^4\ H^{10}\ O$. They equally support the ideas advanced by M. Laurent, that alcohol being the vinic acid of water, the ordinary æther must be its neutral æther, and contain the carbon in two forms, as shown by the following formulæ :—

$$C^2\ H^4 + H^2\ O \text{ and } 2C^2\ H^4 + H^2\ O,$$

Alcohol. Æther.

or $OEtH$ and OEt^2.

Alcohol. Æther.

I digested at a gentle heat in a retort an intimate mixture of sulphovinate of potash, dried at 176° F. *in vacuo*, and potash-alcohol obtained by the action of potassium upon absolute alcohol. I obtained

* Phil. Mag. for November 1850.

† The equivalents employed by the author are retained.

in this manner a highly volatile liquid, which from its properties I recognized to be ordinary æther. We have—

$$SO^4\left(\begin{matrix}H\\C^2H^4\end{matrix}\right)K + C^2H^5(K)O = SO^4K^2 + C^2H^5\left(\begin{matrix}H\\C^2H^4\end{matrix}\right)O.$$

Sulphovinate of pot. Potash-alcohol. Sulph. pot. Æther.

This experiment led therefore to the important fact, that 1 equiv. of alcohol is able to fix the elements of 1 equiv. olefiant gas, to furnish 1 equiv. æther. I then made the same experiment, substituting sulphomethylate of potash for the sulphovinate; I obtained a substance which was gaseous at the ordinary temperature (72°), and which I was unable to condense from want of ice. I found that the gas thus obtained was inflammable, very sparingly soluble in water, and possessed a peculiar ætherial odour; it was evidently the mixed æther—

$$C^3H^8O = \left(\begin{matrix}C^2H^4\\C\ H^2\end{matrix}\right) + H^2O = OMeEt.$$

The preceding results led me quite naturally to prepare similar mixed æthers with the polybasic acids. I have commenced with the carbonic and oxalic acids, and shall soon add succinic acid to them.

By distilling the carbomethylate and oxalomethylate of potash with sulphovinate of potash, I obtained two new æthers, which belonged to the æthylic and methylic series. The reaction is easily explained by the following equations:—

$$CO^3\left(\begin{matrix}H\\CH^2\end{matrix}\right)K + SO^4\left(\begin{matrix}H\\C^2H^4\end{matrix}\right)K = CO^3\left(\begin{matrix}H\\CH^2\end{matrix}\right)\left(\begin{matrix}H\\C^2H^4\end{matrix}\right) + SO^4K^2.$$

Carbomethylate. Sulphovinate. Carborinomethylide.

$$C^2O^4\left(\begin{matrix}H\\CH^2\end{matrix}\right)K + SO^4\left(\begin{matrix}H\\C^2H^4\end{matrix}\right)K = SO^4\left(\begin{matrix}H\\CH^2\end{matrix}\right)\left(\begin{matrix}H\\C^2H^4\end{matrix}\right) + SO^4K^2.$$

Oxalomethylate. Sulphovinate. Oxalovinomethylide.

Casting a glance at the following table, it will be impossible to avoid considering, with M. Gerhardt, water and the sulphuric, carbonic and oxalic acids, &c. as bibasic compounds, whatever theory be adopted to formulate the æthers:—

Hydric acid..... OHH	Carbonic acid..... CO^3 HH
Hydrate of potash .. OKH	Carbonate of potash CO^3 HH
Alcohol ..... OEtH	Carbovinic acid .... CO^3 EtH
Potash alcohol..... OEtK	Carbovinate potash.. CO^3 KEt
Æther..... OEtEt	Carbonic æther .... CO^3 EtEt
Mixed æther ..... OEtMet	Do. mixed ..... CO^3 EtMet
Potash..... OKH	Carbonate of potash CO^3 KK.

Comptes Rendus, October 7, 1850.

On the Ammoniacal Compounds of Platinum. *By* C. Gerhardt.

On reflecting on the remarkable compounds which ammonia forms with the protochloride of platinum, I have frequently asked

myself whether it might not be possible to obtain, with the bichloride of this metal, a parallel series, the terms of which should present sufficient stability to allow of double decomposition after the manner of salts, as with the platinum compounds described by M. Reiset. There is, it is true, the binammoniacal bichloride, the chloride of the interesting series of M. Gros, which behaves like the ammoniacal protochlorides; but it presents differences, which appear at first sight to exclude all parallelism between the two ammoniacal series. In fact, all the salts of M. Gros are chlorinated, whilst the two bases of the salts of M. Reiset contain no chlorine. Recently M. Raewsky has enriched the history of platinum with a new series of similar compounds, which however would correspond to an unknown chloride of platinum, and, what is most remarkable, to one superior to the bichloride.

What connexions exist between all these salts? What relations do they present with the two ammoniacal series of the protochloride? Such are the questions which I propose to solve in this memoir.

A simple comparison has enabled me to fill up an important gap in the series of the platinum compounds. Calling to mind the mode of formation of M. Gros's series by chlorine and one of M. Reiset's chlorides, I thought that the monoammoniacal bichloride ought to be obtained by means of chlorine and the other ammoniacal chloride of the same chemist. Experiment has fully confirmed my suppositions. This new chloride, which forms lemon-yellow octahedrons, is quite as remarkable in its reactions as the ammoniacal protochlorides. It experiences double decomposition with the other salts, and does not liberate ammonia when boiled with potash. When treated with nitrate of silver, chloride of silver and an ammoniacal nitrate of platinum, in which the ammonia is quite as much concealed as in the salts of M. Reiset, are obtained.

This ammoniacal nitrate yields by double decomposition other similar salts. Lastly, I have obtained, in the free and crystallized state, the platinum alkali contained in these new salts. It is precipitated by the addition of potash or of ammonia to their solution.

I have not restricted myself to the investigation of this first series of platinum salts. In order that the parallel might be complete between these salts and the compounds of M. Reiset, it was further requisite to discover salts of a second series containing the same elements plus ammonia; it was likewise necessary to determine, in this respect, the nature of the compounds of MM. Gros and Raewsky.

My numerous experiments have enabled me, I think, to solve these questions in a satisfactory manner. I obtained a nitrate of the second series by acting with nitric acid on the corresponding nitrate of M. Reiset; and with this new nitrate I procured other salts by double decomposition. The salts of MM. Gros and Raewsky are formed by the same base; they are double salts with two acids, one of which is hydrochloric acid. This is easily proved when hydrochloric acid is added to my neutral nitrate; the chloride of M. Gros is precipitated. When this chloride is heated with nitrate of silver,

the nitrate of M. Raewsky is produced. Lastly, when hydrochloric acid is added to the nitrate of M. Raewsky, the chloride of M. Gros is again precipitated. Owing to the kindness of M. Pelouze, who placed at my disposal a specimen of the nitrate prepared by M. Raewsky himself, I have been able to assure myself of the complete identity of that salt and my product obtained by double decomposition. In my memoir I have pointed out the errors on which the formulæ given by the Russian chemist are based.

In my opinion, my new salts, as also the compounds of MM. Gros and Raewsky, are to the deutoxide of platinum what the compounds of MM. Reiset and Peyrone are to the protoxide of that metal. All these salts contain distinct alkaloids, which represent ammonia, in which a part of the hydrogen is replaced by platinum.

According to the general theory of the ammoniacal compounds given by M. Laurent, the platinum salts of M. Reiset contain ammonia, in which 1 equiv. of hydrogen is replaced by its equivalent of platinum, Pt, that is to say, in the platinose (*platinosum*) salts.

In my new salts, 2 equivs. of hydrogen of the ammonia are replaced by the equivalent of platinum which is contained in the platinic (platinicum, pt=$\frac{1}{2}$Pt) salts, an equivalent which weighs only half that of the platinose. The following formula will show the parallelism of the two series:—

Platinose Ammonia (corresponding to the protoxide of platinum).	*Platinic Ammonia* (corresponding to the binoxide of platinum).
NH^2Pt, platinosammine, 2nd series of Reiset.	$NH\,Pt^2$, platinammine, my new salts.
$N^2H^5\,Pt$, diplatinosammine, 1st series of Reiset.	$N^2H^4\,Pt^2$, diplatinammine, my new salts and those of Gros and Raewsky.

I will now call attention to the question, whether one metal can in reality have two equivalents. It will be observed, that, in applying it to bodies admitted to be simple, I merely generalize a principle admitted to be true by all chemists as regards the compound groups of organic chemistry. In fact, the equivalent CH^2, called methylene, is distinguished from the equivalent C^2H^4, or olefiant gas, which nevertheless contains the same elements combined in different proportions. It is stated to be the same carburet of hydrogen, but differently condensed; and it is this difference of condensation to which is owing the difference in the properties of the two carburets and of their compounds. I reason in the same way in regard to platinum, and the metals in general, for their quality of simple bodies is far from being mathematically proved. I say the platinic compounds contain the *platinicum*, pt=$\frac{1}{2}$Pt, which weighs only half that of the *platinosum*, Pt, occupying the same place in the platinose compounds, exactly as the compounds of wood-spirit contain methylene, CH^2, which is only half the weight of olefiant gas, C^2H^4, occupying the same space in the corresponding compounds derived from alcohol.

Table of the Compounds of Platinammine and Diplatinammine.*

1. *Platinammine.*

Crystallized platinammine	$NH\,pt^2+2aq.$
Bihydrochlorate	$2ClH,\,NH\,pt^2.$
Neutral nitrate	$NO^3\,H,\,NH\,pt^2+2aq.$
Binitrate	$2NO^3\,H,\,NH\,pt^2.$
Neutral oxalate	$C^2\,O^4\,H^2,\,2NH\,pt^2+3aq.$
Bisulphate	$SO^4\,H^2,\,NH\,pt^2.$

II. *Diplatinammine.*

Neutral nitrate	$NO^3\,H,\,N^2\,H^4\,pt^2+aq.$
Sesquinitrate	$3NO^3\,H,\,2N^2\,H^4\,pt^2+aq.$
Sesquihydrochloro-nitrate (nitrate R.)	$\left\{\begin{matrix}2NO^3\,H\\ClH\end{matrix}\right\},\,2N^2\,H^4\,pt^2+aq.$
Sesquinitro-oxalate	$\left\{\begin{matrix}C^2\,O^4\,H^2\\NO^3\,H\end{matrix}\right\},\,2N^2\,H^4\,pt^2+aq.$
Sesquihydrochloro-oxalate (oxalate R.)	$\left\{\begin{matrix}C^2\,O^4\,H^2\\ClH\end{matrix}\right\},\,2N^2\,H^4\,pt^2+aq.$
Sesquihydrochloro-carbonate (carbonate R.)	$\left\{\begin{matrix}CO^3\,H^2\\ClH\end{matrix}\right\},\,2N^2\,H^4\,pt^2+aq.$
Sesquihydrochloro-phosphate (phosphate R.)	$\left\{\begin{matrix}PO^4\,H^3\\ClH\end{matrix}\right\},\,2N^2\,H^4\,pt^2.$
Bihydrochlorate (chlorate G. and R.)	$2ClH,\,N^2\,H^4\,pt^2.$
Bihydrochloro-chloroplatinate	$\left\{\begin{matrix}Pt\,Cl^3\,H\\ClH\end{matrix}\right\},\,N^2\,H^4\,pt^2.$
Bihydrochloro-nitrate (nitrate G. and R. of the mother-liquor)	$\left\{\begin{matrix}NO^3\,H\\ClH\end{matrix}\right\},\,N^2\,H^4\,pt^2.$
Bihydrochloro-sulphate (sulphate G.)	$\left\{\begin{matrix}SO^4\,H^2\\2ClH\end{matrix}\right\},\,2N^2\,H^4\,pt^2.$
Bihydrochloro-oxalate (oxalate G.)	$\left\{\begin{matrix}C^2\,O^4\,H^2\\2ClH\end{matrix}\right\},\,2N^2\,H^4\,pt^2.$
Binitro-oxalate	$\left\{\begin{matrix}C^2\,O^4\,H^2\\2NO^3\,H\end{matrix}\right\},\,2N^2\,H^4\,pt^2.$

Comptes Rendus, August 14, 1850.

On the Preparation of Atropine. By M. Rebourdain.

In a memoir published by MM. Bouchardat and Stuart Cooper in the 'Annuaire de Thérapeutique' for 1849, these chemists describe a process for the preparation of atropine, which yields it in a very pure state, but in extremely small quantity. They observe, that the preparation of atropine cannot be so easy as stated by the authors who have made us acquainted with this vegetable alkaloid, since we know several chemists in France who have tried to prepare it without success; that which is met with in commerce is derived from Germany.

* The names between parentheses, marked G. and R., are those given by MM. Gros and Raewsky.

The following process, which enables us to obtain it in a simple, quick and easy manner, may therefore prove of some service. Fresh Belladonna, collected when just about to flower, after having been well pounded in a marble mortar, is submitted to pressure to extract the juice; this is then heated to 176°–194° F. in order to coagulate the albumen, and filtered. When the juice thus clarified is cold, 4 grms. of caustic potash and 30 grms. of chloroform to the quart are added to it; the whole is then agitated for a minute, and set aside. In the course of half an hour, the chloroform charged with the atropine, and having the appearance of a greenish oil, has subsided; the supernatant liquid is decanted and replaced by a little water; this is then decanted, and the washing continued until the decanted water is perfectly clear. The chloroform solution is then poured into a small tubulated retort, and the distillation carried on in a water-bath until all the chloroform has passed into the receiver. The residue in the retort is digested with a little water acidulated with sulphuric acid, which dissolves the atropine, leaving a green resinous matter; the filtered solution is colourless. In order to obtain the atropine in a state of purity, it is merely necessary to pour the solution into a slight excess of carbonate of potash, to collect the precipitate, and to dissolve it in rectified alcohol. This solution furnishes, on spontaneous evaporation, beautiful groups of acicular crystals of atropine.

When it is impossible to obtain the fresh herb, the carefully-prepared officinal extract may be used. 30 grms. of extract of belladonna, made with the purified juice of this plant, were dissolved in 100 grms. of distilled water; 2 grms. of caustic potash and 15 grms. of chloroform were added to the filtered solution. After having agitated the mixture for a minute, and then left it to settle for half an hour, the chloroform holding the atropine had subsided; it was washed with water three times after the supernatant liquid had been decanted; the chloroform solution, collected upon a watch-glass, weighed 11 grms. This solution, exposed to the air, soon evaporated, leaving a greenish crystalline mass, consisting almost entirely of atropine; digested with acidulated water, this mass, on being mixed with a solution of carbonate of potash, furnished a precipitate which weighed 15 centigrms. It was entirely soluble in rectified alcohol, and furnished, on spontaneous evaporation, beautiful crystals of atropine.

I believe this method may be applied to several other substances containing organic alkaloids; if not an œconomical method of obtaining these products, it may at least serve in many cases for determining quickly the value of certain commercial products.

In an early communication I shall describe a method for quickly ascertaining the commercial value of the Cinchonas, by acting upon a very small quantity of bark; I shall also show, that, by means of chloroform, the least traces of iodine can be detected, and shall point out the advantages which it possesses over that by starch.—*Comptes Rendus*, October 14, 1850.

On the Hydrates of Sulphuric Acid. By V. A. Jacquelain.

Numerous contradictory statements exist as to the freezing-points of the acids with 1 and 2 equivs. of water. The author, in verifying these, has pointed out the precautions which are requisite in determining the freezing-point of viscous liquids, the non-attention to which has given rise to the above contradictions. As a result of these observations, the author was led to compare the crystallization of sulphate of soda from a solution saturated at 212°, with the phænomenon of the freezing of mono- and bi-hydrated sulphuric acid on the one hand, and on the other with the facts observed by M. Donny on the cohesion of liquids.

The author has also prepared with great care the sulphuric acids with 1, 2, 3, 4, 5 and 6 equivs. of water, and has taken their density in order to compare them with those of the same hydrates obtained by slow combustion *in vacuo*. Their resistance to freezing at a temperature of from −4° to −40° F. proves that all these products are true combinations. The combinations obtained by the author by synthesis, and analysed in this memoir, are—

$4SO^3, 3HO$; $SO^3, 3HO$; $SO^3, 4HO$; $SO^3, 5HO$; $SO^3, 5HO$.

Comptes Rendus, October 28, 1850.

Experiments on Dulcine. By V. A. Jacquelain.

The following are the results of the author's investigation:—

1. The action of weak sulphuric acid, of the monohydrated acid, and of Nordhausen acid, has furnished two new acids, forming with baryta neutral soluble salts.

2. The action of potash, of lime, and of potash-lime convert it into butyrate, oxalate and alkaline carbonate, with a considerable disengagement of hydrogen.

3. The action of nitric acid gives rise to acids, forming sparingly-soluble salts with baryta.

4. The action of chlorine furnishes an acid, forming with baryta a neutral viscous salt.

5. The elementary analysis leads to the crude formula $C^{10}\ H^{12}O^{10}$. —*Comptes Rendus*, October 28, 1850.

Observations on Minium. By V. A. Jacquelain.

The author describes in this paper the various modes of action of acetic acid upon minium, and points out the formation of the acetate of minium and of the acetate of the binoxide of lead. The latter is represented, according to analysis, by $3(C^4\ H^3\ O^3)\ PbO^2$; and its decomposition by heat is explained by the production of acetone, of coumarine, the reduction of the oxide of lead and the liberation of a little acetic acid, carbonic acid and water. The examination of the behaviour of acetate of minium towards a solution of ammonia led to the discovery of the sesquioxide of lead, $Pb^2\ O^3$.—*Comptes Rendus*, October 28, 1850.

How to remove Silver Stains from the Skin. *By* A. W. Brieger.

The spot is first brushed over with a solution of iodine in alcohol, immediately afterwards with a moderately-dilute solution of caustic potash, and washed.—*Jahrb. für Prakt. Pharm.*, xx. p. 90.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of Green and Gray Colours from Oxide of Chrome, for Calico Printing. *By* Dr. W. H. de Kurrer.

Greens, prepared from oxide of chrome, for cylinder printing, were first introduced into Bohemia in 1840, and soon became universally employed in printing establishments; and immediately upon their adoption came also into use the numerous tints of pearly-gray, likewise obtainable from oxide of chrome. Colours prepared from oxide of chrome possess the valuable property of resisting the action both of light and air, acids and alkalies, and may consequently be classed amongst the fast colours. In preparing these colours for printing cotton fabrics, the substances employed are principally chloride and nitrate of protoxide of chrome, and chromo-sulphate of potash or chrome-alum. The chloride of chromium, called also sea-green in the Bohemian manufactories, is employed in the following manner in calico-printing establishments, for the purpose of producing the green oxide of chrome. At the commencement of the process, the green hydrate of oxide of chrome is prepared by first dissolving 4 kilogrms.* of bichromate of potash in 22 litres† of boiling water. Then, into a boiler or vessel containing 108 litres of boiling water, 4·5 kilogrms. of pulverized white arsenic are thrown, and boiled for ten minutes; a precipitate will be formed, and must be allowed to settle; the clear liquor is then run off, and immediately mixed with the solution of bichromate of potash, stirring all the time; in a short time the mixture acquires a green tint, and the hydrated oxide of chrome will be formed and precipitated. After being several times well stirred and allowed to cool, the whole is thrown upon a filter of white wool, and the hydrated oxide of chrome remaining on the filter is carefully washed with boiling water. It is then dried, and is ready to be employed for the preparation of the chloride. In order to obtain the latter salt, hydrochloric acid of 22° Beaumé is diluted with water until the acid no longer gives off vapour. It is then heated, and whilst hot, as much of the hydrated oxide of chrome prepared as above is added as will saturate the acid and leave a slight excess of the oxide undissolved. The whole is then left to settle, and the clear liquor is decanted from the undissolved matter. In this state the solution of chloride of chromium still presents some traces of free acid, which would act injuriously upon the fibres of the cotton. To

* About 2 lbs. English. † About a quart English.

remove this, and obtain the product in a neutral state, potash ley (marking 20° Beaumé) is poured in very gradually until the oxide of chrome begins to be precipitated. The solution of chloride of chromium thus prepared, and which is of a dark green colour, is evaporated until it marks 46° Beaumé. After cooling, a colouring matter is obtained from it, consisting of oxide of chrome of the finest green colour. This preparation is sold under the name of sea-green. Before this substance (which can be used with greater advantage than any other preparation for printing in green upon calico) was known, the following, amongst other preparations, were employed for obtaining chrome-green:—

1st Preparation.—To a solution of 0·656 kilogrm. of bichromate of potash in 3 litres of water add 1·406 kilogrm. of hydrochloric acid, and afterwards 0·250 kilogrm. of pulverized tartaric acid. By the addition of the tartaric acid the solution acquires a fine green tint, together with a sweet taste. The following proportions have been given for producing the various shades of colour required:—

	kilogrammes.					
Chromate of potash..	1·750	2·875	1·000	0·500	0·437	0·375
Hydrochloric acid ..	3·125	1·625	1·750	1·000	0·937	0·750
Tartaric acid	2·500	1·625	0·500	0·250	0·172	0·187

All these compounds (which have a slightly acid reaction) are, when used for printing, thickened with starch or wheat-flour, gum-tragacanth or other gums; and, to fix the colours, the printed fabrics are, according to the tint required, kept stretched in the air for several days, and then washed; or they are passed through a bath of chalk or of ammonia. This bath of ammonia is prepared with 24 litres of boiling water, 4 kilogrms. of slacked lime, and 2 kilogrms. of hydrochlorate or sulphate of ammonia, and the fabrics are submitted thereto by being passed several times through a machine similar to that used for printing ground colours, a free current of air being kept up to carry off the pungent odour of the ammonia.

2nd Preparation.—0·500 kilogrm. of bichromate of potash are boiled in 3 kilogrms. of hydrochloric acid until chlorine ceases to be evolved; 0·500 kilogrm. of soda, previously calcined, and 0·500 kilogrm. of caustic soda ley, marking 14° Beaumé, are then added; and for printing, the liquor is thickened with gum-tragacanth. The piece, when printed and dried, is passed through a boiling ammoniacal bath, composed of 0·500 kilogrm. of caustic lime, 0·500 kilogrm. of hydrochlorate or sulphate of ammonia, and 24 litres of water, after which it is well washed, and finally stretched and dried.

3rd Preparation.—To a hot solution of 0·656 kilogrm. of bichromate of potash in 3 litres of water 0·500 kilogrm. of syrup is added, and afterwards by degrees 2 kilogrms. of hydrochloric acid, marking 34° Beaumé, which causes this liquor very shortly to assume a green tint. It is neutralized with caustic soda, the colour is thickened as in the first preparation, and the printed fabric is finished in the same manner.

4th Preparation.—Nitrate of chrome is prepared by dissolving

in nitric acid the green precipitate of oxide obtained by arsenic in the same manner as the chloride is prepared with hydrochloric acid. This green, thus obtained, gives a yellowish tint upon cotton fabrics.

Printing Sea-green with the Roller.—For cylinder-printing with chloride of chromium, the colour must be thickened either with gum-tragacanth or starch. The following is the mode of proceeding:—

1. *Thickening with Gum-tragacanth.*—Take 0·220 kilogrm. of gum-tragacanth reduced to very fine powder, which make into a thin paste with alcohol; then cover up the vessel in which this operation is carried on, and leave it to settle for a few hours; after which add 14·250 litres of solution of chloride of chromium, marking 46° Beaumé; leave the whole for from twenty-four to thirty-six hours, merely stirring occasionally, and finally strain it through a cloth. When the colour is too thick for printing delicate designs from the cylinder, it is only necessary to add more of the solution of chloride of chromium until the desired consistence is attained.

2. *Thickening with Starch.*—Mix intimately 2 kilogrms. of starch with 5 litres of water, boil the mixture to the consistence of glue, let it cool, and add the solution of chloride of chromium, marking 46° Beaumé, until it is of the consistence required for printing.

As gum-tragacanth is of a denser nature than starch, it furnishes bolder and more intense colours than the latter. After printing, the fabrics are stretched on a frame, and left during the night in a cool place; the next day they are treated with caustic potash ley, marking 2° Beaumé, well aired, pressed as dry as possible, and then laid for about an hour in running water, washed with washing wheels, pressed and dried, and finally submitted to the process for brightening the colours.

After fixing the yellow, green and blue colours by passing them through lime or by immersion in the bath of acid chromate of potash, the operation is completed; the brightest possible green is obtained by passing the fabric through a bath of acetate of copper, as a portion of the green chromate of copper then combines with the chrome-green, and heightens its tone. The operation is conducted as follows:—The proper quantity of water is heated, in a suitable vessel, to a temperature of 131°–133° F., 2 litres of a solution of acetate of copper are added, and the printed pieces are passed twice backwards and forwards through the liquor; they are then placed in running water; after which the moisture is pressed out of them, and they are dried. When six pieces have been passed through the copper-bath in the manner described, 2·375 kilogrms. of solution of copper are added for each successive piece, and this is continued so long as there are any pieces to operate upon. The salt of copper gives to the green colour a peculiar lustre, without having an injurious influence over the other colours present; even the chrome-yellow loses none of its beauty. The acetate of copper is prepared by dissolving 20 kilogrms. of sulphate of copper or blue vitriol in 72 litres of water, decomposing by 10 kilogrms. of sugar of lead, and using the clear supernatant liquor.

Printing with two Green Colours.—When, by means of a reserve of arseniate of potash, figures dyed red or violet by madder are stopped out, and the white parts of the fabric printed by hand from a design in relief, with a solution of chloride of chromium thickened with starch or gum-tragacanth, then, by afterwards printing over this with sea-green, by means of the cylinder, a dark green pattern will be obtained upon a light gray ground; and after applying the other colours requisite for completing the design, the fabric is passed through a bath of acetate of copper to brighten the greens.

Cylinder-printing with Yellow Designs upon a Green Ground.—Yellow patterns upon a green ground may be produced by printing (after applying the reserve to protect the madder-reds and purples) with the base of lead, and afterwards applying the chrome-green with the printing-roller. Fabrics thus treated are passed through milk of lime at a temperature of 100° F.; they are washed and dried, and then the fast blue, green and yellow colours are printed; the fabrics are again passed through milk of lime, and, after being well washed, the yellow and green colours are brought out by a bath of acid chromate of potash.

The preparation of lead for this purpose consists of the following composition:—3 kilogrms. of pipe-clay are damped with 1·780 litre of water, and mixed with 3·560 kilogrms. of gum-water, to which is added 1·440 kilogrm. of a solution of chloride of zinc. For every litre of this solution, 0·150 kilogrm. of acetate of lead, dissolved in a small quantity of water, is added before printing.

Chrome-olive.—Very fine and fast olive colours may be obtained suitable for cylinder-printing (upon which yellow patterns may be produced by acetate of lead) by means of the following preparations:—

1. *Light Olive.*—To 12 litres of solution of chloride of chromium thickened with starch add 2 litres of catechu-brown.

2. *Medium Olive.*—To 12 litres of solution of chloride of chromium thickened with starch add 2·350 litres of catechu-brown.

3. *Dark Olive.*—To 12 litres of solution of chloride of chromium thickened with starch add 3·560 litres of catechu-brown.

The catechu-brown, which is added to the oxide of chrome or sea-green to form olive colours, is prepared by dissolving 2·5 kilogrms. of Gambia catechu in 10 litres of water over a gentle fire, and straining the decoction through a fine sieve; 2·375 litres of this solution are then boiled with 0·150 kilogrm. of starch, 0·090 kilogrm. of verdigris and 0·120 kilogrm. of sal-ammoniac.

The day after printing, the olive colours may be brought to any desired shade by the following means:—

1. To produce a brown tint, the pieces are introduced into a vat furnished with a drum, and containing milk of lime (at a temperature of 104° F.), and afterwards carefully washed. 2. In order to approach nearer to an olive-green, instead of milk of lime, they are passed four or five times over the drum (a single piece at a time, and in one direction only), through a bath of acid chromate of potash. 3. When it is desired to bring the above colours to a

more decided green, the pieces, after having received all the colours required, viz. the yellow, the fast blue and green, and also the sea-green, are passed through a bath of acetate of copper heated to 140° F.

Cylinder-printing in Green by means of Arseniated Chloride of Chromium.—Shades of green may be obtained, differing somewhat from the ordinary sea-green, by the employment of arseniated chloride of chromium, prepared in the following manner:—In a large earthen vessel a mixture of 4 kilogrms. of hydrochloric acid and 9 litres of water are heated to ebullition on a sand-bath; to the liquor is added 3 kilogrms. of bichromate of potash. When the solution is complete, 3·650 kilogrms. of finely-pulverized white arsenic are introduced in small quantities, in order that the liquor may not rise and overflow. When the arsenic is likewise completely dissolved, the solution is allowed to cool. The clear liquor, when decanted, is kept ready for use.

For immediate use, 1 kilogrm. of starch and 0·060 kilogrm. of finely-powdered gum-tragacanth are boiled in 8 litres of water, and the mixture is allowed to cool. Into 8 litres of this thickening mixture, 32 kilogrms. of arseniated chloride of chromium are slowly poured, and when properly mixed, 6·5 kilogrms. of potash ley of 16° Beaumé are added very gradually, stirring briskly all the time. The colour appears very thin before the addition of the potash; but it is thereby thickened and rendered suitable for cylinder-printing. The fabrics printed with this preparation are the next day passed through a weak potash ley (heated to 140° F.), to which a small quantity of milk of lime has been added; they are then well washed, stretched and dried.

To produce a fast green colour approaching to gray, take 12 litres of green printing colour, and 2·375 litres of fast blue prepared from indigo; mix them together, print the fabrics therewith, and next day pass them through milk of lime, wash with clean water, and stretch and dry them as before.

In order to *impregnate* the fabric with the colour by means of the cylinder machine, so as to produce a uniform green ground, mix gradually 71 litres of the solution of arseniated chloride of chromium, marking 55° Beaumé, with 6·500 kilogrms. of solution of potash, of 16° Beaumé, diluted with about 15 litres of water; then add 3 kilogrms. of mucilage of gum-tragacanth, and 0·040 kilogrms. of chloride of iron, and 0·067 kilogrms. decoction of logwood, of 2° Beaumé.

Pearl-gray Colour for Printing.—This pleasing colour is obtained by means of sulphate of chrome and of potash (chrome-alum). It is prepared in the following manner:—Into four large stone vessels are severally poured 2 kilogrms. syrup of sugar and 2 kilogrms. of thick gum-water, prepared by dissolving 1·50 kilogrm. of gum in 1·25 litre of water. Into each vessel a hot solution of 2 kilogrms. of bichromate of potash in 6 litres of water is then poured, the mixture being briskly stirred. After being allowed to cool down to 86° F., 2·50 kilogrms. of colourless sulphuric acid

diluted with water (say 2 kilogrms. acid and 3 litres water) are added, again stirring briskly. After the lapse of a short time the liquor will become spontaneously heated and rise rapidly. In order that no loss may arise, the liquor which may overflow should be received in another vessel. The colour gradually changes from orange to olive-green, and finally to dark gray. It must be stirred from time to time until the liquor ceases to froth up, when it will be found to have acquired a fluid consistency and a blackish-gray colour. As soon as the rising ceases, that which had overflowed is poured back again, and when perfectly quiescent and cold the contents of the four pots are mixed together, when the liquor will be ready for use, it being found to consist of a compound or mixture of sulphate of chrome, with sulphate of chrome and potash (chrome-alum).

This colour will be found well adapted for cylinder-printing, which is performed in the ordinary manner of printing with starch colours, viz. by introducing a cylinder provided with a woollen band into the dye-vat, from which the colour is fed to the engraved cylinder. Ten pieces of calico may be easily printed off with this colour without changing the doctors, as they are not affected by it.

The next day after printing the fabrics are stretched upon frames, and immersed during six minutes in a vat filled with milk of lime; they are then left for an hour in running water, and passed through a bath of hot water to dissolve all the reserve, in order that this may be completely washed out in the washing machine, and they are afterwards dried.

Green Patterns upon a Pearl-gray Ground.—These may be obtained perfectly fixed by preserving the madder-reds and violets with the reserve of arseniuret of potassium, then printing on the white ground the patterns in sea-green, and afterwards with the cylinder applying the pearl-gray colour.

Yellow Patterns on a Pearl-gray Ground.—These are produced with the preparation of lead, in the same manner as above described for sea-green.

Yellow, green, blue and catechu-brown colours may be advantageously applied to the above; and in passing through a bath of milk of lime and another of yellow and neutral chromate of potash, the yellow and green will be brought out and the catechu-brown fixed.

The bath of neutral chromate of potash, for bringing out and fixing the colours, is prepared in the following manner:—Into a vat, provided with a drum, and three parts filled with water, a solution of 3 kilogrms. of neutral chromate of potash is poured, to which are added not more than from 4·750 litres to 5 litres of vinegar, in order that it may not be acid, as bichromate or acid chromate of potash would convert the pearl-gray into chromate of chrome, which is of a brownish-yellow colour. The yellow, to be good, should appear in the bath of neutral chromate of potash of a brimstone colour, the green having always, on the contrary, a pear-green tinge; consequently, in printing in pearl-gray, should a fine grass-green be required, a good steam colour must be resorted to.

Pearl-gray approaching to Blue.—To produce this colour, the sulphate of chrome and potash must be prepared as follows:—In 6 litres of water, 4 kilogrms. of bichromate of potash, in small pieces, are dissolved; 2·5 kilogrms. of colourless sulphuric acid are diluted with 2 litres of water, and this dilute acid, when cold, is poured slowly into the solution of chromate, which is stirred; then add 2 kilogrms. of powdered sugar, in small portions at a time, which addition will cause an elevation of temperature and great effervescence. When the mixture is cold, the sulphate of chrome and potash possesses a certain degree of consistence; and, for printing, the following proportions of syrup and British gum are added as thickening matter:—1st, 2·375 litres of syrup are diluted with 2·375 litres of water, and added to 4·750 litres of solution of chrome-alum; 2nd, 3 kilogrms. of British gum are boiled in 3 litres of water, and after complete cooling are poured into 4·750 litres of the solution of chrome-alum. Neither dry gums nor gum-water will serve as thickeners for this colour, as gums contract and form with the double sulphate of chrome and potash a hard matter resembling leather. The printed fabrics are next day passed through milk of lime, and treated in the manner above mentioned. If to 12 litres of the pearl-gray about 1 litre of the catechu colour, prepared in the same manner as for chrome-olive, be added, a peculiar reddish-gray colour will be produced.

Chrome-green Printing Colour.—A very fine green colour (suitable for printing stripes upon cotton) may be produced by preparing chloride of chromium in the following manner:—4 kilogrms. of pulverized white arsenic are dissolved in 106 litres of water by the application of heat; 3·5 kilogrms. of bichromate of potash are also dissolved by heat in 14 litres of water, and this solution is poured slowly (stirring continually) into the arsenious solution. After cooling, the green precipitate is thrown upon a cloth, and when well drained, 5 kilogrms. of hydrochloric acid of 22° Beaumé are added to it; it is then dissolved in a sand-bath, and evaporated to 4° Beaumé, neutralized by means of 1·750 litre of soda ley at 20° Beaumé, stirring continually; and, finally, the liquor is thickened with 100 grms. of gum-tragacanth, finely powdered, when it will be fit for printing. The fabrics thus printed are left for twenty-four hours in a cool place, and then dried.

Steel Green-gray Steam Colour.—To prepare this colour, which is chiefly employed for printing cotton stripes, the chrome-alum is prepared as follows:—Into a solution of 7·5 kilogrms. of bichromate of potash in 15 litres of water pour slowly 4·625 kilogrms. of colourless sulphuric acid, and mix gradually with the liquor 1·875 kilogrm. of raw sugar. The stone vessel in which this solution is effected is kept hot in a sand-bath until the mixture has acquired an emerald-green colour, when it may be left to cool.

Colour for Printing.—To 2·375 litres of starch-paste, prepared with 0·360 kilogrm. of that substance, are successively added 7·125 kilogrms. of chrome-alum, 9·5 kilogrms. of catechu-gray, and 0·900 kilogrm. of acetic acid of 3° Beaumé.

To prepare the catechu-gray, dissolve 4 kilogrms. of Gambia cate-

chu in 24 litres of wood-spirit, and add 1·780 litre of gum-water for each 1·780 litre of the catechu solution. The gray colour is finally obtained by the addition of 0·060 kilogrm. of green vitriol.

This colour requires most particularly to be steamed, as the green and other steam colours, which are easily affected, would be changed by the acetic acid, which is otherwise carried off in the form of steam.—Newton's *Journal*, August 1850.

On a new and ready Method of ascertaining whether a Substance is coloured by Vermilion. *By* Dr. Bolley.

When vermilion is mixed with a solution of nitrate of silver containing an excess of caustic ammonia, it immediately turns black. This colour, which at first is merely superficial, soon pervades the whole mass, especially on trituration in a dish. The effect of the ammoniacal solution of silver is so powerful, that the reaction occurs as quickly with colours in which vermilion is one of the constituents as with pure vermilion. Sealing-wax, which is coloured red with vermilion, turns almost instantly black on being moistened with this solution, and likewise varnish containing vermilion. This reaction may consequently be successfully employed for ascertaining whether a red pigment contain vermilion; none of the other red colours with which I am acquainted exhibit anything similar. In order to ascertain what were the products of this decomposition, I triturated an excess of the vermilion with solution of silver and caustic ammonia for a long time, poured the whole upon a filter, and then continued the washing for some time with water and ammonia. The liquid which passed through left on evaporation a white salt, in which nitric acid, peroxide of mercury and ammonia were readily detected; but the amount of the peroxide of mercury varied in successive repetitions of the experiment; and at last it was found that the white residue consisted of a mixture of those salts which have been prepared and examined by Kane, Soubeiran, Mitscherlich and Pagenstecher, and are obtained by precipitating solutions of the pernitrate of mercury with ammonia. These salts consist of amidide of mercury with variable quantities of pernitrate of mercury. Three different salts of this kind are enumerated by L. Gmelin in his Manual:—

$$HgNH^2 + 5HgO, NO^5$$
$$HgNH^2 + 3HgO, NO^5$$
$$HgNH^2 + 2HgO, NO^5.$$

The one is converted by excess of ammonia into the other, which readily explains why in the above new mode of formation the same salt is not always obtained.

The black residue upon the filter was again triturated with solution of silver and ammonia, in order to remove entirely the vermilion contained in it; and this in general succeeded, excepting a very small quantity. The residue proved to be sulphuret of silver.

The reaction results even with strongly-diluted solutions of silver, so that vermilion deserves to be mentioned as a sensitive reagent for salts of silver when they are mixed with ammonia.—Liebig's *Annalen*, August 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Hippuric Acid, and the Products of its Oxidation, by Peroxide of Lead. By Dr. H. SCHWARTZ.

1. *Amorphous Modification of Hippuric Acid.*—Hippuric acid is characterized, both in the isolated state and in its salts, by a great tendency to crystallization. Liebig's observation, therefore, that hippuric acid is deposited from alcohol, after some months' standing, in cauliflower-like masses, appeared remarkable. In the preparation of hippuric æther, I accidentally obtained the same amorphous hippuric acid in a tolerably pure state, and submitted it to analysis. I had dissolved very pure beautifully-crystallized hippuric acid in boiling absolute alcohol, and then saturated it with muriatic acid gas. On dilution with water, the hippuric æther fell to the bottom as an oil; it was purified by recrystallization and very dilute boiling alcohol. The cauliflower-like masses of the hippuric acid were deposited from the mother-liquors. This exhibited a perfectly amorphous appearance under the microscope. A few short crystals were mixed with it. It dissolves pretty readily in boiling water without previously melting, and separates on cooling unaltered. The aqueous solution has a distinct acid reaction. It dissolves very readily in ammonia, especially on the application of heat; muriatic acid precipitates crystalline hippuric acid from the solution. The ammoniacal solution likewise gives, on being mixed with nitrate of silver and heated to boiling, the beautiful crystalline silver salt of hippuric acid. The substance, dried over sulphuric acid, parts with no water at 212°. The following are the results of the analyses which were made with oxide of copper, a spiral of sheet copper being inserted in the front portion of the tube, and a current of oxygen employed towards the end of the operation :—

Carbon.....	60·27	60·45	18 =	108	60·33
Hydrogen	5·25	5·50	9	9	5·02
Nitrogen	7·88	..	1	14	7·82
Oxygen	..	..	6	48	26·83

2. *Double Salt of Hippurate and Benzoate of Baryta.*—A mixture of hippuric and benzoic acids was accidentally obtained. In order not to lose the whole of the hippuric acid, I tried to separate them

by means of the baryta salts. According to a statement in Löwig's Organic Chemistry, benzoate of baryta crystallizes in needles, and is very sparingly soluble in water; and I knew that the hippurate of baryta is a very readily soluble salt. The mixture of the two acids was therefore saturated with barytic water, the solution treated with carbonic acid, boiled, filtered and evaporated. It was however only after considerable concentration that some light silvery laminæ subsided, which proved on analysis to be benzoate of baryta. The salt lost, on being dried at 212°, 8·30–8·28 per cent. water. The dry salt gave 44·23 C, 2·87 H and 40·76 BaO per cent. The formula $C^{14} H^5 O^3 + BaO$ requires 44·31 C, 2·63 H and 40·41 per cent. BaO; 2 equivs. water correspond to 8·67.

Subsequently some hippurate of baryta, in rhombic prisms with a waxy lustre, crystallized out; they gave on analysis 30·89 per cent. BaO. $\overline{Hi} + BaO$ requires 31·06.

When the mother-liquor had been evaporated nearly to the consistence of a syrup, some peculiar dull warty masses, which appeared to consist of concentric groups of dendritic crystals, separated. On being decomposed with muriatic acid. they furnished a mixture of benzoic and hippuric acids. By carefully selecting the crystals, and repeated recrystallization, the compound was at length obtained pure. At the same time a mixture was made of 1 equiv. benzoic and 1 equiv. hippuric acid, dissolved in water, and saturated with barytic water. The clear solution likewise deposited at first some benzoate, then hippurate of baryta, but finally furnished a pretty large amount of the double salt. It gave on analysis—

Carbon	43·43	43·41	..	32	=192	43·13
Hydrogen	3·55	3·64	..	14	14	3·14
Nitrogen.....	3·61	..	..	1	14	3·14
Oxygen	..	..	..	9	72	16·17
Baryta	34·18	34·29	34·25	2	153·2	34·42
Water.....	7·56	7·43	..	4	36	7·48

The formula therefore is $BzO^3 + \overline{Hi} + 2BaO + HO + 4Aq$. I did not succeed in obtaining an analogous silver salt when the acids mixed in equivalents were neutralized with ammonia, a deficiency of nitrate of silver added, and the precipitate recrystallized from hot water: the laminar crystals obtained left on ignition 46·97 per cent. of silver; the benzoate of silver contains 47·15 Ag. It was therefore pure benzoate of silver.

3. *Products of Oxidation of Hippuric Acid by Peroxide of Lead.*

A. *Benzamide,* $C^{14} H^7 NO^2$.—This interesting body was discovered by Liebig, and prepared by a very tedious process from oil of bitter almonds. As is well known, Fehling was the first to discover the production of benzamide from hippuric acid; he assumed that hippuric acid consisted of benzamide and fumaric acid—

$$C^{14} H^7 NO^2 + C^4 HO^3 = C^{18} H^8 NO^5.$$

Benzamide. Fumaric acid. Hippuric acid.

But this explanation was no longer tenable after the discovery of Dessaignes, that hippuric acid is decomposed by ebullition with strong acids or alkalies into benzoic acid and glycocoll. Benzamide must therefore originate from the pre-existing benzoic acid and the ammonia liberated in the oxidation of the glycocoll, with the elimination, it is true, of 1 atom of water in an aqueous solution; whilst no method is yet known of producing benzamide from benzoic acid by dry ammonia, even with the assistance of absolute alcohol. All my experiments for this purpose were of no avail; even on dissolving benzoic æther in alcohol, saturating it with dry ammonia, and heating this liquid in a sealed glass tube to 212° in a water-bath, I did not obtain a trace of benzamide. Dumas, Malaguti and Leblanc nevertheless obtained benzamide from benzoic æther by heating it with an aqueous solution of ammonia above 212°. I was therefore induced to study more minutely the formation of benzamide from hippuric acid.

Hippuric acid was triturated, according to Fehling's directions, with peroxide of lead, water poured over it, and then heated to boiling in a broad dish or large flask. Much carbonic acid was disengaged. The hippuric acid gradually dissolved, and a large quantity of hippurate of lead was formed, just as stated by Fehling, which on the slightest cooling separated, especially on the surface, in crystals. The lead salt was decomposed by sulphuric acid; sulphate of lead subsided, which mixed with the peroxide at the bottom, giving to it a light chocolate colour.

The boiling, careful addition of sulphuric acid, &c., was continued until even an excess of peroxide of lead seemed to produce no further decomposition. As soon as the operation was finished, the liquid was filtered while hot from the residual peroxide and sulphate of lead. On cooling, it in general deposited some hippuric acid, and then furnished a white crystalline mass on evaporation. On slow evaporation, distinct crystals were immediately obtained.

On redissolving the mass in a little boiling water, a small quantity of a white shining substance, nearly insoluble in water, remained (see p. 473). On cooling, as well as on further evaporation, white indistinct crystals separate, which appear under the microscope in the form of curved needles. No mention of this form of crystallization of benzamide is made in any of the former investigations; and as some analyses made with substance, which was probably mixed with hippuric acid, did not furnish the numbers of benzamide, I at first imagined I had to do with a new substance. However, by frequent recrystallization, I obtained not only concordant results, but also crystals which corresponded in form with those of benzamide.

Most beautiful and pure crystals of benzamide were obtained from a dilute ammoniacal solution, and likewise from a very dilute solution of caustic potash. If the solution is sufficiently concentrated, it congeals on cooling to a solid mass, consisting of silky, white, shining needles; they soon however become converted, as stated by Fehling, into large, shining, quadratic prisms, which can be recognized with the naked eye. If a drop of a concentrated so-

lution of benzamide be placed under the microscope, the slender needles are seen to shoot out rapidly; but very soon the large square prisms, which consist apparently of an aggregation of several smaller ones, are observed to form among the needles which dissolve.

On recrystallization from water, the needles are never obtained, but only the square prisms. At first I avoided the use of ammonia, and also the presence of free acid, from its being stated of benzamide, that it is most readily converted into benzoic acid and ammonia by acids and alkalies. However, further experiment soon taught me, that small quantities of acids and alkalies have no decomposing action, or at all events an exceedingly slow one, upon benzamide. It is entirely decomposed by concentrated solution of caustic potash, and also by very long ebullition with muriatic acid.

Benzamide melts on being heated to about 212°, and solidifies on cooling to a crystalline mass*. A few degrees above its melting-point it begins to evaporate, and distils over nearly unaltered, but the residue turns brown, and on analysis no longer furnishes correct results. It was therefore always dried between 158° and 176° F.; and as in this state it was too bulky to be weighed off in the tray, it was mixed in the mortar with some warm oxide of copper, and then filled into the tube; the rest of the tube was filled with fused oxide of copper. Benzamide, dried over sulphuric acid, loses no water between 158° and 176°. The following are the results of the analyses:—

Carbon.....	69·55	69·50	68·44	69·42	14	=84	69·42
Hydrogen ..	6·34	5·92	5·86	6·11	7	7	5·78
Nitrogen	11·29	11·23	11·11	..	1	14	11·56
Oxygen	..	..	..	..	2	16	13·24

When benzamide, both that crystallized from water as well as that from dilute ammonia, was evaporated with muriatic acid only, a portion of it was converted into benzoic acid and ammonia. It is remarkable that nearly always one-third of the entire amount of ammonia was found by precipitation with chloride of platinum. It seemed therefore as if the generated benzoic acid protected the remainder of the benzamide from decomposition; however, on boiling benzamide for an hour and more with concentrated muriatic acid, and constantly renewing it, the whole of the nitrogen of the benzamide was obtained as chloride of ammonium, so that this decompostition might be employed for estimating the nitrogen, instead of combustion with soda-lime.

Benzamide has no smell, and a slightly bitter aromatic taste.

When pure benzamide is submitted to the action of peroxide of lead and water, it experiences, even on long ebullition, no further change; but if some sulphuric or nitric acid is added and the whole boiled, it is slowly oxidized; it passes into a peculiar body, which causes the colourless liquid filtered from the peroxide of lead to turn brown on the addition of ammonia and exposure to the air, and deposits a brown humus-like sediment. It is my intention to submit this substance to further examination.

* Pure benzamide melts at 239° F.—Ed.

B. *Hipparaffine*, $C^{16}H^{8}NO^{2}$.—I have already stated, when describing the preparation of benzamide, that, on recrystallizing the crude product from hot water, a silky crystalline mass, nearly insoluble in hot water, was left behind. The benzamide of the second or third crystallization also left some of this peculiar body on being dissolved in as little hot water as possible. It was readily soluble in boiling alcohol, and could therefore be likewise easily extracted from the residue of peroxide and sulphate of lead by this medium. On cooling, it crystallized from it in excessively minute silky needles.

I had observed that this substance, which I had hitherto obtained only in very small quantity, was principally formed when I had accidentally added a slight excess of acid in the precipitation of the oxide of lead by sulphuric acid. I therefore tried to oxidize the hippuric acid by peroxide of lead and a larger amount of sulphuric acid; and was not a little rejoiced, when, with a very gentle heat, after a very violent disengagement of carbonic acid, the entire mass suddenly became solid by the formation of the silky needles.

The same compound is also obtained when phosphoric acid is substituted for the sulphuric acid.

The employment of peroxide of lead and nitric acid gave a still more favourable result. Muriatic acid, on the contrary, liberated chlorine, which escaped unaltered. The operation was now carried out on a large scale. I found that a very considerable excess of peroxide of lead and sulphuric acid was requisite, but only a gentle heat. Having once heated it too quickly, I obtained only benzoic acid; the glycocoll had been eliminated from the hippuric acid, and had been oxidized separately.

The pasty mass was brought while hot upon a filter, and washed with hot water till not a trace of acid was contained in it. The filtered solution deposited on cooling some hipparaffine, and furnished crystals of benzamide on evaporation, especially when the free acid had been neutralized with ammonia; and in case nitric acid had been employed, the oxide of lead had been removed by sulphuric acid or sulphuretted hydrogen. If it had not been heated sufficiently long, or too little acid had been used, less hipparaffine was formed, whilst a large amount of unaltered hippuric acid was present, but always with a small quantity of benzamide.

The residue was now dried upon the filter, removed from it, powdered, and exhausted with strong boiling alcohol, of which too little must not be used, in order that the separating hipparaffine may not stop up the filter. It was filtered as quickly as possible, and the residue upon the filter washed with boiling alcohol.

The united alcoholic liquids furnished, on cooling and on further evaporation, very beautiful fascicles of silvery-white needles, which were very bulky, but amounted to very little by weight. There also remained much alcohol in the intervening spaces, so that in the drying there is danger of the whole substance being again dissolved upon the filter; it must therefore be dried between paper over sulphuric acid. It cannot be washed thoroughly with alcohol, as this also dissolves the substance too quickly in the cold. The best me-

thod of purifying it is allowing it to dry, rubbing it to powder, then exhausting it with boiling water, and washing it upon the filter for some time with hot water; a little ammonia may also be added to the water, especially to remove any admixture of hippuric acid. The aqueous filtered solution deposited a very small quantity of hipparaffine in slender needles. The small solubility of hipparaffine in water appears partially to be owing to its not being moistened by that liquid, resembling in this respect arsenious acid; at all events it is deposited from the aqueous solution obtained in its preparation in comparatively larger quantity.

The substance used for analysis burnt without any residue; it was generally dried over concentrated sulphuric acid, and finally at 212°, without losing any water; it consequently contains no water of crystallization:—

Carbon.....	71·75	71·33	71·31	71·36	16=96		71·64
Hydrogen ..	6·08	5·97	6·21	..	8	8	5·97
Nitrogen	10·75	10·79	10·06	..	1	14	10·45
Oxygen	..	..	..	..	2	16	11·95

leading to the formula $C^{16} H^{8} NO^{2}$.

Hipparaffine is very soluble in æther, from which however it crystallizes in a confused mass. From its softness it is difficult to powder. The reaction, both of the alcoholic as well as of the hot aqueous solution, is perfectly neutral. From its sparing solubility, hipparaffine has neither taste nor smell. It is neither more nor less soluble in ammonia, dilute muriatic acid or sulphuric acid, than in pure water. An aqueous solution of caustic potash has no action upon it; an alcoholic solution of potash dissolves it readily, but it is again separated unaltered by water.

Only when fused with hydrate of potash does hipparaffine disengage ammonia, but a large portion is constantly left undecomposed, and separates unaltered on being mixed with water. On ignition with soda-lime, the whole of the nitrogen is expelled in the form of ammonia, besides which a quantity of benzole passes over. It forms a colourless solution with concentrated sulphuric acid in the cold, which turns slightly brown on being heated. On the addition of much water, the hipparaffine is separated nearly unaltered.

It dissolves pretty readily in concentrated nitric acid upon the application of heat, but without evolution of gas, and separates on cooling unaltered, especially on the addition of water. Red fuming nitric acid dissolves it in the cold, the substance at the same time melting like an oil. As long as it has not been boiled, water separates the greater part unaltered; but, on being heated, some gas appears to be disengaged, and then an addition of water no longer causes a precipitate.

Peroxide of lead alone or with acids, bichromate of potash with or without sulphuric acid, solution of iodine, chlorate of potash and muriatic acid, produce no essential alteration. Hipparaffine melts at about 392° F., and then solidifies to a crystalline mass; at a higher temperature it distils over unaltered in part, whilst the re-

mainder is coloured black; it burns in the air with a luminous fuliginous flame, and leaves a small quantity of an easily-combustible cinder.

The formula $C^{16} H^8 NO^2$ is merely the empirical expression of the analyses. It was not possible to confirm it by any products of decomposition or compounds. I therefore endeavoured to show its relation to the phænomena which occur in the oxidation of glycocoll and the formation of benzamide. I have still to mention, that, both in the preparation of benzamide, and especially in the preparation of hipparaffine, a peculiar substance is volatilized, which strongly irritates the eyes and lungs. On condensing the water which distilled over, it had a slightly acid reaction, and on being mixed with ammonia reduced nitrate of silver; it was therefore probably formic acid, but I was not able to demonstrate this. The irritating odour did not disappear on saturating the liquid with potash.

4. *Products of Decomposition of Glycocoll.*—The decomposition of glycocoll by potash in a state of fusion was especially important; I can only confirm the results of Horsford. Much hydrogen and much ammonia are given off, and the residue contains cyanide of potassium and oxalate of potash. I am induced however to interpret this decomposition in a somewhat different manner to what Horsford has done. Glycocoll is simply decomposed by hydrate of potash into

$C^2 \quad O^3$	oxalic acid
$C^2 N \quad H$	prussic acid
H^3	hydrogen
$C^4 H^4 NO^3$.	

The ammonia is only a secondary product, resulting from the decomposition of the cyanide of potassium by excess of hydrate of potash—

$$C^2 NKa + 5HO = C^2 O^4 + NH^3 + 2H + KO.$$

It might, it is true, be also admitted that glycocoll is directly decomposed by the oxidizing influence of the hydrate of potash into

$$C^2 O^3 + C^2 O^4 + NH^3 + 5H = C^4 H^4 NO^3 + 4HO*.$$

The phænomena of the decomposition which glycocoll experiences when heated with peroxide of lead and dilute sulphuric acid are perfectly analogous; a lively effervescence results, owing to the escape of carbonic acid, and pure prussic acid distils over. The residue contains a considerable amount of sulphate of ammonia, formed either by the partial decomposition and oxidation of the prussic acid, or in a direct manner from the glycocoll. The more prussic acid distils over the less ammonia is there in the residue, and *vice versâ*—

$$C^4 H^4 NO^5 + 4O = C^2 NH + 2CO^2 + 3HO.$$

The 2 atoms CO^2 are derived from the $C^2 O^3$ by the addition of 1 atom O—

$$C^2 NH + 3HO = C^2 HO^3 + NH^3.$$

* I may observe that I have never succeeded in producing the cherry-red colour said to arise on heating glycocoll with a concentrated solution of potash.

The formic acid however does not pass over, but at the moment of its production is oxidized by the addition of 2O into CO^2+HO.

If, on the other hand, glycocoll is heated with peroxide of lead and pure water, a very remarkable decomposition takes place. A strongly ammoniacal water distils over, and carbonate of lead remains—

$$C^4\,H^5\,NO^5+6O=4CO^2+HO+NH^3.$$

A trace of CyH appears however to be also formed at the commencement. The distillate, for instance, reduces nitrate of silver on the application of heat, giving rise to a beautiful metallic mirror; it consequently most probably contains formic acid, produced by the decomposition of the prussic acid by water. This phænomenon is the more remarkable, since it would be believed that in this case the residue should contain either formiate of lead or cyanide of lead; but this is not so, for the residue yields no formiate of lead on being exhausted with boiling water; the little oxide of lead which is found in the filtered solution appears to be combined with a trace of undecomposed glycocoll. The washed residue likewise furnishes, on distillation with dilute sulphuric acid, no prussic acid; it contains therefore no cyanide of lead—a further reason why no formic acid should occur in the distillate. However, it is well known that carbonic acid expels prussic acid from its salts; it was therefore possible that had some cyanide of lead been formed, the carbonic acid had decomposed it, and the prussic acid which had distilled over was resolved into formic acid and ammonia. At all events the greater portion of the nitrogen passed over as ammonia. As it was possible that the alkaline distillate contained some of those bases resembling ammonia, for instance methylia, ($C^4\,H^5\,NO^4=C^2\,H^5\,N+2CO^2$); it was saturated with muriatic acid, evaporated to dryness with chloride of platinum, and the small yellow octohedra washed with absolute alcohol and æther. Dried at 212° and weighed, it furnished on ignition 43·62–43·56 per cent. platinum; the ammonio-chloride of platinum contains 44·36 per cent. of platinum; it was consequently pure ammonia, which had distilled over.

All these three modes of decomposition of glycocoll lead consequently to the following result. It seems as if two groups of atoms existed in glycocoll, viz. $C^2\,O^3+C^2\,H^5\,N$; in the first case the oxalic acid enters into combination with the potash, in the second and third it is oxidized into carbonic acid, with this sole difference, that in the second case it is expelled by the more powerful sulphuric acid, whilst in the last it remains combined with the oxide of lead. The residue, $C^2\,H^5\,N$, is easily resolved either into $C^2\,NH$ and H^3, or into NH^3 and $C^2\,H$, or formyle. The latter is converted by oxidizing agents into formic acid, $C^2\,HO^3$, by 3O, or into $2CO^2$ and HO by 5O.

Horsford's statement, that glycocoll is decomposed by evaporation with dilute sulphuric acid into $C^2\,O^3$ (the formation of which, it is true, has not been demonstrated), and into a compound, $C^2\,H^2\,O+NH^4\,O+SO^3$, points to the pre-existence of this group.

When, in the latter, no attention is paid to the sulphuric acid, it may be written $C^2 H^4 N + 2HO$. Perfectly analogous relations occur in the oxidation of hippuric acid by peroxide of lead, with or without the addition of acid. The hippuric acid is to be considered in the anhydrous state as a combination of glycocoll with benzoic acid, minus water. Benzoic acid, minus water, may be compared with lactide, the anhydrous lactic acid minus water. I shall denote this hypothetical compound, $C^{14} H^4 O^2$, by the name of *benzide*. With the assumption of benzide in hippuric acid, it is readily explained why no hippuric acid can be reproduced from benzoic acid and glycocoll. When the benzide has assimilated water and become benzoic acid, the combination can only result by the vital force. In accordance with this, I designate benzamide by the expression *benzide-ammonia*, $C^{14} H^4 O^2 + NH^3$. This does not originate, like the other amides, by the distillation of the benzoate of ammonia, because in benzoic æther it contains no benzoic acid, but benzide. But it is formed on treating the chloride of benzoyle with ammonia. This is benzide + chloride of hydrogen; when dissolved in water, benzoic acid is formed from the benzide and hydrochloric acid set free.

It is further formed in a very simple manner from hippuric acid. When glycocoll is oxidized by peroxide of lead and water, it gives $4CO^2$ and NH^3; the latter unites with the liberated benzide to form benzide-ammonia or benzamide.

Hipparaffine, $C^{16} H^8 NO^2$, is formed from the hippuric acid by the removal (and oxidation) of $C^2 O^3$.

$$\begin{array}{l} C^{18}\ H^8\ NO^5 \\ \underline{C^2 \qquad\quad O^3} \\ C^{16}\ H^8\ NO^2 \end{array}$$

It may be viewed as $C^{14} H^4 O^2 + C^2 H^4 N$, *i. e.* benzide + the second group of atoms of the glycocoll. The benzide protects this group from further oxidation by its union with it.—Liebig's *Annalen*, August 1850.

On the Amount of Potash existing in the Blood.
By C. Enderlin, M.D.

The investigations of M. Liebig, in which he showed that soda and chloride of sodium preponderate in the blood, whilst potash and the chloride of potassium exist in excess in the liquid of the flesh, are well known. It will also be recollected, that the same chemist found lime the predominating earth of the blood, whilst magnesia prevailed in the liquid of the flesh.

The investigations of M. Enderlin, as the following table shows, are in strict accordance with those of M. Liebig; in one case only did he find the quantity of potash so great (in the blood) as to approximate to that of the liquid of the flesh. This deviation from the rule appeared sufficiently important to induce the author to repeat his analysis, which he was enabled to do, in consequence of having preserved some of the blood of the female from whom it was

taken. The result was confirmed. The woman from whom the blood had been removed had been delivered four months previously, and had ceased to suckle for a month, on account of an affection of the breasts. It is important to mention this, because it appears, as will be shown presently, that the anomaly observed was intimately connected with this circumstance.

The following table exhibits the proportion of the amount of potash to that of soda (including the chloride of sodium) in the ash of various kinds of blood.

Assuming the soda as =100, he found in the—

	Soda.	Potash.	
Ash of the blood of a man ..... for	100	6·5	
... ... an ox, I.....	100	13·5	0·736 metallic chloride yielded no platino-chloride of potassium.
... ... an ox, II.	100	5·5	
... ... a sheep	100	0·0	
... ... a calf	100	44·3*	
... ... a pigeon, I.....	100	43·9	
... ... a pigeon, II.	100	46·8	
Ash of the serum of a woman in the 6th month of pregnancy	100	1·6	
Ash of the serum of the same woman, $1\frac{1}{2}$ month before delivery	100	1·2	
Ash of the serum of the same woman, 4 months after delivery	100	3·8	
Ash of the cruor of the same woman, 4 months after delivery	100	418·0	Analysed in 1844.
Ash of the cruor of the same woman, 4 months after delivery	100	354·0†	Analysed in 1847.

Some of the chloride of potassium must have been volatilized on heating the alkaline chlorides to redness; hence the difference.

Henneberg obtained in the—

	Soda.	Potash.
Ash of the blood of the fowl ..... for	100	40·8
.. ... the ox.....	100	5·9
... ... the horse.....	100	9·5

The proportion of the lime to the magnesia in the ash of the above blood was also different, and, in fact, the quantity of magnesia was increased. I found—

	4 months *after* delivery.		$1\frac{1}{2}$ month *before* delivery.
	I.	II.	
Lime	1·62	1·63	2·44
Magnesia.....	1·62	1·57	0·70

The quantity of iron was increased, whilst that of the chloride of sodium exhibited a diminution after delivery.

* In young animals, the quantity of potash in the blood appears constantly greater according to my experiments.

† The greater part of the alkali of the blood is combined with chlorine, and becomes transferred to the serum; so that we cannot conclude upon the composition of the ash of the whole of the blood from the analysis of the ash of the clot.—Ed. Liebig's *Annalen*.

On the analysis of the ash of the whole blood, I found—

	I. In the 6th month of pregnancy.	II. 1½ month before delivery.	4 months after delivery.
Peroxide of iron ..	8·64	8·05	16·20
Chloride of sodium..	58·43	62·96	57·12

The quantity of potash in the whole blood was not determined, and the chlorine found was calculated as chloride of sodium.

M. Liebig has shown that the food of animals is not everywhere of the same composition in regard to the quantity of potash and soda contained in it, thus *e. g.* wheat, barley, oats, edible roots and foliaceous plants in the Odenwald, Saxony and Bavaria, contain salts of potash only, none of soda. The excess of potash in the blood of this woman could not be explained from the nature of the food*.

M. Enderlin regards the abnormal composition of this blood as explicable from a consideration of the physiological condition of the woman, the period of formation of the milk, which so abounds in salts of potash, &c., as also in the condition of the infant undergoing development, which requires such large quantities of salts of potash (and of magnesia) for the formation of its tissues, especially the flesh.—Liebig's *Annalen*, August, 1850.

On the Action of Chlorine and Bromine on Propylene, Æthylene, and their Homologues. *By* A. Cahours.

In his beautiful researches on the æthers, M. Regnault has shown that olefiant gas, when submitted to the action of chlorine, furnishes two series of compounds, belonging the one to the group $C^4 H^4$, the other to the group $C^4 H^6$, the ultimate terms of which are, for the first, $C^4 Cl^4$, and for the second, $C^4 Cl^6$.

The action of a dark red heat upon the acids of the group $C^m H^m O^4$, and on the corresponding alcohols, producing, as I have recently shown, propylene, $C^6 H^6$, a gas polymeric with olefiant gas, which may be obtained in considerable quantity by observing certain conditions of temperature, I have been led to study the action of chlorine upon this gas, with a view to establish two series parallel with the above-mentioned.

When a current of chlorine, and the gases derived from the decomposition of pelargonic, æthalic, or any other acid of this series, are passed into a large flask with three tubulures, one of which is drawn out into a point, and terminates in a flask serving as receiver, a reaction takes place, which is rendered perceptible by the appearance of white fumes. If the current of gas is well regulated, the greenish-yellow colour of the chlorine is never perceptible, and the sides of the flask become coated with a limpid liquid, which collects in the receiver. The principal product is a liquid which boils be-

* Strecker has lately published some important experiments, which may be noticed here. He found that the bile of some sea-fishes, which live in a medium so abundant in soda, contained mostly potash (choleate of potash), whilst the bile of the ox, an animal the food of which contains mostly potash with some amount of soda, yielded mere traces of potash on incineration.

tween 219° and 221° F., has an ætherial odour analogous to that of the Dutch liquid, and whose composition may be expressed by the formula $C^6 H^6 Cl^2$. This is the compound discovered by Captain Reynolds *, by acting with chlorine upon the gaseous products resulting from the igneous decomposition of amylic alcohol. The action of chlorine upon this substance should necessarily furnish a series of derivatives analogous to that obtained from the Dutch liquid; and I consequently submitted the preceding product to the successive action of chlorine, and succeeded, by operating upon large quantities, in obtaining the following series:—

$C^6 H^5 Cl^3$, boiling at	219°,	D=1·151=4 vols. of vapour.
$C^6 H^5 Cl^3$, ...	338°,	1·347	...
$C^6 H^4 Cl^4$, between 383° and	392°,	1·548	...
$C^6 H^3 Cl^5$, between 428° and	437°,	D=	...
$C^6 H^2 Cl^6$, between 464° and	473°,	D=1·626	...
$C^6 H Cl^7$, boiling at	500°,	D=1·731	...

and, as final product, the chloride of carbon—

$C^6 Cl^8$, boiling at 536°, D=1·860=4 vols. of vapour.

This compound is, as will be seen, the homologue of the perchlorinated acetene (Faraday's sesquichloride of carbon), $C^4 Cl^6$.

The preceding terms, when submitted to distillation with an alcoholic solution of potash, furnish an analogous series to that derived from the Dutch liquid and its products of substitution, viz.

$C^6 H^5 Cl$ =4 vols of vapour.		$C^6 H^3 Cl^4$=4 vols. of vapour.	
$C^6 H^4 Cl^2$	...	$C^6 H Cl^5$	...
$C^6 H^3 Cl^3$	...	$C^6 Cl^6$	...

Captain Reynolds likewise found that bromine forms with propylene the compound $C^6 H^6 Br^2$. By the successive action of an alcoholic solution of potash and bromine, I have obtained a series corresponding to the preceding, viz.

$C^6 H^6 Br^2$, boiling at	293°,	D=1·974=4 vols. of vapour.
$C^6 H^5 Br$, ...	144°,	D=1·472	...
$C^6 H^5 Br^3$, ...	378°,	D=2·336	...
$C^6 H^4 Br^4$, ...	439°,	D=2·469	...
$C^6 H^3 Br^5$, ...	491°,	D=2·601	...
$C^6 H^4 Br^2$, ...	248°,	D=1·950	...
$C^6 H^3 Br^3$.			

The easy production of these compounds induced me to examine the successive action of an alcoholic solution of potash and bromine on the brominated Dutch liquid, in the hope of obtaining the two bromides of carbon $C^4 Br^4$ and $C^4 Br^6$. But although I have operated upon 225 grms. of the brominated Dutch liquid, I have not succeeded, the derivatives of the product $C^4 H^4 Br^2$ being more altered by the alcoholic solution of potash in proportion as they contained a larger amount of bromine; besides the bromide of potassium and the brominated term of the inferior series, salts of potash, formed by brominated acids, are produced, to which I shall

* Page 217 of the present volume.

return on some future occasion. I nevertheless obtained the two series—

$C^4\ H^4\ Br^2$	$C^4\ H^3\ Br$
$C^4\ H^4\ Br^3$	$C^4\ H^2\ Br^2$
$C^4\ H^2\ Br^4$	$C^4\ H\ Br^3$
$C^4\ H\ Br^5$	

I have likewise examined the action of bromine upon some of the substances which are polymeric with olefiant gas and propylene, such as butylene, amylene, oleene, paramylene, and obtained—

$C^8\ H^8\ Br^2$ and $C^8\ H^7\ Br$

$C^{10}\ H^{10}\ Br^2$, $C^{10}\ H^9\ Br^3$ and $C^{10}\ H^9\ Br$, $C^{10}\ H^8\ Br^2$

$C^{12}\ H^{12}\ Br^2$

$C^{16}\ H^{16}\ Br^2$

$C^{20}\ H^{20}\ Br^2$

On casting a glance at the preceding results, it is seen that all the terms of the first series correspond to a suite of carbonated hydrogens represented by the general formula $C^m\ H^{m+2}$, which may be considered as the group whence are derived the simple æthers or their isomers, whilst the terms of the second series, which may be represented by the general formula $C^m\ H^m$, are the homologues of olefiant gas.

M. Melsens, in his important investigations relative to the substitutions of hydrogen by chlorine, has shown that the chloride of carbon, $C^2\ Cl^4$, might be brought back to the state of marsh gas, $C^2\ H^4$, passing successively through the intermediate members, $C^2\ HCl^3$, $C^2\ H^2\ Cl^2$, $C^2\ H^3\ Cl$.

M. Regnault having demonstrated, on the other hand, that the Dutch liquid, and its isomer monochlorinated hydrochloric æther, furnish, under the influence of chlorine, a series of isomeric products of which only the ultimate terms are identical, it would be worth while applying Melsen's method of inverse substitution to these compounds, as it ought to lead to the gas $C^4\ H^6$, passing through the intermediate term $C^4\ H^5\ Cl$. This latter substance, which presents the composition of hydrochloric æther, must be isomeric, but not identical with it, if we take as basis the fact, that the different products of these two series are merely isomeric, and do not become identical until the final product is reached. At all events it would be curious, if we succeeded in obtaining the products $C^4\ H^5\ Cl$ and $C^4\ H^5\ Br$ from chlorinated and brominated Dutch liquid, to compare them with the hydrochloric and hydrobromic æthers, and to endeavour afterwards to obtain a series of isomeric compounds of the different simple æthers. If we bear in mind that M. Hofmann succeeded in regenerating alcohol by acting with caustic potash upon hydrobromic æther, we may hope to obtain a compound isomeric with alcohol, and subsequently other corresponding compounds. I am at present engaged with M. Wurtz in submitting these hypotheses, which can only be considered as *jeux d'esprit* until they have been confirmed by experiment, to further examination.—*Comptes Rendus*, Aug. 26, 1850.

On the Distillation of Mercury by high-pressure Steam.
By M. VIOLETTE.

This new process for the distillation of mercury, consists in immersing the mass to be distilled in a current of the vapour of water, heated from 350° to 400° centigrade: the vapour acts at once as the heating agent and mechanical agent; it first heats the metal so as to produce distillation, and then drives before it and draws the mercurial vapour, the reproduction of which it facilitates; it hastens the distillation, just as a hot current of air increases the evaporation of water; the aqueous vapours, charged with mercurial vapour, are condensed together in a common refrigeratory; the metal separates at the bottom of the receiver, while the condensed water occupies the upper part. It is curious to observe the liquid thread which flows from the refrigeratory; two currents or threads are distinguishable, an upper one which is water, and below is the mercurial thread; there is a continuous current of both. No concussions occur, and the operation goes on as quietly and as easily as the distillation of water.

The apparatus employed by the author in these experiments, consists of,—1st, a cast iron cylindrical retort, receiving the vessel which contains the mercury; 2ndly, an iron worm, which, being heated, the vapour of water circulates in it, and being heated to a proper degree, enters the retort, traverses it from one end to the other, the mercury being immersed in it; it then escapes, with the mercurial vapour, and both are condensed in a refrigeratory.

The author gives in a series of tables the results which he has obtained by a series of experiments relating to the distillation of mercury, both alone and amalgamated; he states the quantity of vapour necessary, and the œconomical advantages of the new process, which he thus details:—

1. *Facility of the Operation.*—Simple ebullition and the distillation of water are substituted for the difficult and dangerous distillation of mercury; in which there is more trouble in managing the fire, more danger of breakage of the apparatus, more difficulty in removing the metal, more wear of the retort; whereas in the new process the temperature is constant and fixed, and much lower than the red heat usually employed.

2. *Œconomy of Operation.*—One workman alone can manage an apparatus charged with 1000 kilogrammes of amalgam; the new process is adapted even to larger dimensions.

3. *Œconomy of Fuel* is certain, and practice alone can state the amount of it; no useless expenditure of fuel will occur, since the heat employed will not be greater than required for the distillation of the metal.

4. *Œconomy of Mercury.*—The distillation of 100 kilogrammes of silver amalgam occasions the loss of two kilogrammes of mercury. There are produced and annually distilled six millions of amalgamated silver; there is therefore a loss of 120,000 kilogrammes of mercury, worth at least one million of francs, which loss the new process avoids.

5. *Public Health.*—In the new process there is no loss of mercury;

the mercurial vapour is condensed with the vapour of water; further, in the common operation, mercurial vapour fills the whole of the apparatus, and when it is opened at the close of the operation, the vapour is diffused in the atmosphere; whereas in the new process the vapour has driven all metallic vapour from the apparatus, and there is no danger in opening it. Thus the operation is complete, and the employment of high pressure steam seems to have effected the long-sought solution of the problem, of perfectly preserving the workmen from the mortal attacks of mercury in the numerous and important uses in which this metal is distilled.—*Comptes Rendus*, Octobre 14, 1850; and *Philosophical Magazine* for December.

On the Action of Bases upon Salts. By M. Alvaro Reynoso.

It is generally admitted that when a salt, the oxide of which is insoluble, is treated with an alkaline solution, the oxide is precipitated without redissolving, unless in its uncombined state it is soluble in an excess of the alkali with which the salt containing it is mixed.

On investigating the action of potash and soda on the arsenites, the author observed some facts, which, if they be not precisely contrary to the general law which he has cited, prove at least that this phænomenon of precipitation is sometimes intimately connected with the nature of the salt above the precipitate; so that, in certain cases, this salt may determine the solubility of the oxide.

Thus, for example, the oxides of copper, uranium, cobalt, nickel, silver, mercury and sesquioxide of iron, being insoluble in potash and in soda, when these alkalies are poured into the arsenites of these bases, precipitation of the insoluble oxide ought merely to occur, with the formation of arsenite of potash or soda, unaccompanied with any action on the oxide; M. Reynoso has, however, found that the arsenites of all these oxides are completely soluble in potash, although in a separate state they are insoluble.

Arsenite of iron is very soluble in potash; the solution of arsenite of copper is blue, and after a certain time it decomposes into protoxide of copper, which precipitates, whilst the arsenite of potash becomes arseniate.

The decomposition of the solution of arsenite of mercury is almost instantaneous. The solution of silver is colourless, and decomposes very slowly, precipitating silver as a black powder. This solution does not precipitate with chloride of sodium; on the contrary, chloride of silver, which is insoluble in potash, dissolves in it very readily when arsenite of potash is added.

M. Reynoso took advantage of these two properties of arsenite of silver to effect the reduction of the salts of palladium by means of silver. The experiment is performed as follows: chloride of palladium, to which arsenite of potash is previously added, is poured into a solution of arsenite of silver in potash. A black powder is readily precipitated, which contains metallic silver and palladium. Chloride of platina is much more readily reduced than that of palladium.

It is to be observed, that in these reactions, arsenite of silver decomposes much more quickly than when it is alone.

The arsenites of cobalt, nickel and uranium, dissolve completely in potash and soda, only in the nascent state. For this purpose it is necessary to employ arsenite of potash with a great excess of potash, and to pour this solution into a soluble salt of cobalt, nickel or uranium.

These reactions will be readily understood, by admitting that arsenite of potash is capable of forming a double soluble salt with the compound of potash and these oxides, and that it is under this influence that their solution is effected. When potash is made to act upon an insoluble salt, the oxide of which is itself soluble in an excess of potash, a solution can only occur on the condition of the formation of a soluble double salt. Thus, for example, the author has stated that arsenite of lead is insoluble in potash. The proof that these reactions depend upon the nature of the salt formed is, that arsenite of lead, which is insoluble in potash, is completely soluble in soda.

When potash is added to an insoluble salt, it first combines with the acid, and the oxide set free will remain without acting upon the salt formed; but if excess of potash be added, and the oxide is soluble in it, then if the compound of this oxide with potash cannot unite with the supernatant salt, two soluble salts will be present, which, being able to form an insoluble salt by their decomposition, will regenerate the primary salts. This, however, is a very rare case; for experiment has proved that almost all the salts of potash have the property of forming a soluble double salt with the oxides soluble in potash.

With respect to ammonia, the author has stated the solubility therein of arsenite of sesquioxide of iron.

In concluding, M. Reynoso observes that four cases of the action of potash on insoluble salts may occur:—

1. In the case of certain oxides, which, when uncombined, are soluble in potash, and which form soluble double salts with all the salts of potash, the solution may be observed under all circumstances.

2. In some cases, uncombined oxides, which are soluble in potash, will form salts insoluble in potash when the acid is not such as yields a soluble double salt with the compound of the oxide and potash.

3. Some other uncombined oxides, insoluble in potash, may nevertheless sometimes form a soluble double salt, and they will consequently dissolve, when, in the nascent state, they are put into contact with potash, in the presence of the salt of potash with which they can combine.

4. When the oxide is insoluble in the alkalies, it precipitates without redissolving, when the salt which it contains is treated with an excess of alkaline base. This last case happens when the oxide precipitated cannot form a soluble double salt.—*Comptes Rendus*, Juillet 15, 1850.

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